

CHAPTER 1

Genesis and evolution in the chemistry of organogermanium, organotin and organolead compounds

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The task of science is to induce the future from the past

Heinrich Herz

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I. INTRODUCTION

Germanium, tin and lead are members of one family, called the silicon subgroup. Sometimes these elements are called mesoids as well, due both to their central position in the short version of Mendeleev's Periodic Table and to their valence shells, which occupy an intermediate place among the I–VII Group elements¹. They can also be called the heavy elements of Group 14 of the Periodic Table.

The history of the silicon prototype of this family and its organic derivatives is elucidated in detail in the literature^{2–5}. In contrast, we could not find any special accounts dealing with the history of organic germanium, tin and lead compounds. The only exception is a very brief sketch on the early history of the chemistry of organotin compounds⁶. Some scattered information on the organic compounds of germanium, tin and lead can be found in some monographs and surveys. In this chapter we try to fill the gaps in this field.

Humanity first encountered the heavy elements of Group 14 at different times; with germanium, it happened quite unusually in the middle of the 19th century. As with the discovery of the planet Neptune⁷, which was first predicted by astronomers and almost immediately discovered, Mendeleev, who predicted the existence of three hither to unknown elements, reported at the Russian Chemical Society session on December 10, 1870 on the discovery of one of these elements as follows: ‘. . .to my mind, the most interesting among undoubtedly missing metals will be one that belongs to Group IV and the third row of the Periodic Table, an analog of carbon. It will be a metal, following silicon, so we call it ‘*eca-silicon*’⁸. Moreover, Mendeleev even predicted the physical and chemical properties of the virtual element^{9–12}. Having no conclusive proof of the existence of *eca-silicon*, Mendeleev himself began experimental investigations aimed at finding it in different minerals¹³. It is noteworthy that as early as 1864 Newlands¹⁴ and Meyer¹⁵ suggested the possible existence of an element like *eca-silicon* and predicted its atomic weight. However, Mendeleev was the first to predict properties of the element in detail.

Fifteen years later the German chemist Winkler^{16,17}, working at the Freiberg Academy of Mines, was able to isolate during the investigation of a recently discovered mineral argirodit (Ag_6GeS_5) a new element in its free state. Initially, Winkler wanted to

name the new element neptunium, after the newly discovered planet Neptune. However, this name seemed to be given for another falsely discovered element, so he called the new element germanium in honor of his motherland^{18–21}. At the time several scientists sharply objected to this name. For example, one of them indicated that the name sounded like that of the flower Geranium while another proposed for fun to call the new element Angularium, i.e. angular (causing debates). Nevertheless, in a letter to Winkler, Mendeleev encouraged the use of the name germanium. It took same time until the identity of *eca*-silicon and germanium was established^{18–22}. Polemics, as to which element germanium is analogous flared up ardently. At first, Winkler thought that the newly discovered element filled the gap between antimony and bismuth. Having learned about Winkler's discovery, almost simultaneously in 1886 Richter (on February 25, 1886) and Meyer (on February 27, 1886) wrote him that the discovered element appeared to be *eca*-silicon. Mendeleev first suggested that germanium is *eca*-cadmium, the analog of cadmium. He was surprised by the origin of the new element, since he thought that *eca*-silicon would be found in titanium–zirconium ores. However, very soon, he rejected his own suggestion and on March 2, 1886, he wired Winkler about the identity of germanium and *eca*-silicon. Apparently, this information raised doubts in Winkler's mind about the position of germanium in the Periodic Table. In his reply to Mendeleev's congratulation he wrote: '...at first I was of the opinion that the element had to fill up the gap between antimony and bismuth and coincide with *eca*-stibium in accordance with your wonderful, perfectly developed Periodic Table. Nevertheless, everything showed us we dealt with a perfectly well developed Periodic Table. But everything implied that we are dealing with *eca*-silicon²³. The letter was read at the Russian Physical and Chemical Society section on March 7. Winkler reported that the properties of the element and its common derivatives corresponded closely to those predicted for *eca*-silicon. A second letter by Winkler was read in a Chemical Section meeting of the Russian Physical and Chemical Society on May 1, 1886. Winkler reported that the properties of germanium and its simpler derivatives were surprisingly very similar to those predicted for *eca*-silicon^{22,24}. This is reported in Winkler's paper in the Journal of the Russian Physical and Chemical Society entitled 'New metalloid Germanium', translated into Russian at the author's request^{25,26}.

An inspection of Table 1 impresses one by the precise way in which Mendeleev predicted the properties of germanium and its elementary derivatives.

In 1966, Rochow²⁷ somewhat criticized the accuracy of Mendeleev's predictions of the properties of *eca*-silicon (germanium). He stated: 'Mendeleev predicted that *eca*-silicon would decompose steam with difficulty, whereas germanium does not decompose it at

TABLE 1. The properties of *eca*-silicon (Es) and its derivatives predicted by Mendeleev^{9–12,19,20} in comparison with the properties of germanium and several germanium derivatives^{24–30}

| Properties | M = Es | M = Ge |
|---|---------|--------|
| Atomic weight | 72.0 | 72.3 |
| Specific weight | 5.5 | 5.469 |
| Atomic volume | 13.0 | 13.2 |
| Specific weight of MO ₂ | 4.7 | 4.703 |
| B.p. of MCl ₄ | ca 90° | 88° |
| Specific weight of MCl ₄ | 1.9 | 1.887 |
| B.p. of M(C ₂ H ₅) ₄ | ca 160° | 160° |
| Specific weight of M(C ₂ H ₅) ₄ | 0.96 | 1.0 |

all. This is to say that germanium is less metallic than was predicted. Mendeleev also said that acids would have a slight action on the element, but they have none; again it is a more negative element than was predicted. There are many more chemical facts³¹ which point in the same direction: germanium is more electronegative than was expected by interpolation, and it actually behaves a great deal like arsenic'. Rochow was right to some extent. It is known^{32,33} that in accordance with Mendeleev's predictions germanium has more metallic characteristics than silicon; in a thin layer or under high temperatures germanium reacts with steam, and it reacts very slowly with concentrated H_2SO_4 , HNO_3 , HF and Aqua Regia. In relation to the Allred and Rochow electronegativity scale^{34,35} the electronegativity of germanium is higher than that of silicon. However, according to other scales^{36–39} and to Chapter 2 of this book, the electronegativity of germanium is lower or approximately the same as that for silicon. As illustrated in Table 1 Mendeleev predicted not only the possibility of existence, but also the properties of the simple organogermanium derivative Et_4Ge .

It is noteworthy that Winkler synthesized Et_4Ge in 1887^{23,29}. Its properties were consistent with those predicted by Mendeleev. Organogermanium chemistry was born at this time.

In contrast to germanium the exposure of mankind to tin and lead was much earlier and not so dramatic^{18–21,28}. These two elements belong to the seven main elements known to ancient man⁴⁰. Up to the seventeenth century, tin and lead were often confused, as is witnessed by their Latin names, i.e. Plumbum album, Plumbum candidum (Sn) and Plumbum nigrum (Pb). Tin was known in countries of the Near East at least from the middle of the third millennium BC. Lead became known to the Egyptians at the same time as iron and silver, and very probably earlier than tin^{19,28}.

Many of Mendeleev's predecessors (Pettenkofer, Dumas, Cooke, Graham and others) assumed that tin and lead cannot belong to the same group as silicon¹² and Mendeleev was the first to include them in the same group of his Periodic Table with silicon and *eca*-silicon. He made this courageous prediction based on the assumption that the unknown element *eca*-silicon should have properties intermediate between metals and nonmetals and that all these elements, including carbon, should belong to one group.

The forefather of the chemistry of organic compounds of tin and lead was the Swiss chemist Carl Löwig. In the middle of the nineteenth century in the Zurich University laboratory (which was not set up to handle toxic compounds), he developed for the first time several methods for the synthesis of common organic derivatives of these two elements and described their properties^{41–44}.

Following Edward Frankland, who paid attention to organotin compounds as early as 1853⁴⁵, Löwig became one of the founders of organometallic chemistry but, unfortunately, historians of chemistry have forgotten this. In spite of his work with rather toxic organotin and organolead compounds during a period of several years in the absence of safety precautions, Löwig lived a long life and died only in 1890 due to an accident.

It is necessary to outline the nomenclature that we use before starting to develop the genesis and evolution of the chemistry of organic derivatives of heavy elements of Group 14. From the moment of their appearance and to some extent up to now, the names of organic derivatives of tin and lead were based on the name of the corresponding metals. It should be mentioned that tin and lead are called quite differently in English, German, French and Russian — Tin, Zinn, Etein, Олово, and Lead, Blei, Plomb, Свинец, respectively. In addition, archaic names of these compounds (such as trimethyltin oxide and alkylgermanium acid) are incompatible with the modern nomenclature of organosilicon compounds, which are the prototypes of this mesoid group. In this chapter we use the nomenclature of organic compounds of germanium, tin and lead approved by IUPAC⁴⁶ in analogy with the nomenclature of organosilicon compounds, based on their Latin names (Germanium,

Stannum, Plumbum). It is not the central metallic atom that is named, but only its hydride MH_4 (germane, stannane, plumbane) and the substituents which replace hydrogen atoms in the hydride molecule. Compounds in which the metal atom valence is either higher or lower than 4 are named in analogy to the nomenclature of organosilicon compounds.

In this chapter, we have tried to gain some insight into the genesis and development of the chemistry of organic germanium, tin and lead compounds up to the end of the 20th century. We have also paid attention to the work of the early researchers which was sometimes forgotten in spite of their tedious work under more difficult conditions than in the present time, which laid the fundamental laws of the chemistry of organic germanium tin and lead compounds. The organic chemistry of the heavy elements (Ge, Sn, Pb) of the silicon sub-group has been previously reviewed extensively either in reviews devoted to organic derivatives of all these elements^{1,47-73} or in separate reviews on organogermanium⁷⁴⁻⁸⁶, organotin⁸⁷⁻¹⁰⁶ and organolead compounds¹⁰⁷⁻¹¹².

Valuable information can be also found in chapters devoted to organometallic compounds¹¹³⁻¹²³ and in many surveys¹²⁴⁻¹³⁸. Excellent bibliographical information on reviews devoted to organogermanium (369 references)⁷⁹, organotin (709 references)¹⁰⁰ and organolead compounds (380 references)¹¹² have been published in Russia. Unfortunately, all the literature cited did not review the historical aspect, so our attempt to extract from that vast body of information the chronological order of the genesis and development of the organic chemistry of germanium tin, and lead compounds was not an easy task. It forces us to re-study numerous original publications, in particular those published in the 19th century. Nevertheless, the references presented in chronological order still do not shed light on the evolution of this chemistry, but they have important bibliographic value.

II. ORGANOGERMANIUM COMPOUNDS

A. Re-flowering after Half a Century of Oblivion

Up to the middle of the 20th century organogermanium derivatives were the least understood among the analogous compounds of the silicon subgroup elements. As mentioned above^{23,29} the first organogermanium compound, i.e. tetraethylgermane, was synthesized for the first time by Winkler in 1887 by the reaction of tetrachlorogermane and diethylzinc^{23,29}, i.e. a quarter century later than the first organic compounds of silicon, tin and lead were obtained.

The synthesis of Et_4Ge proved unequivocally that the germanium discovered by Winkler belong to Group IV of the Periodic Table and that it was identical to Mendeleev's *eka-silicon*. Consequently, Winkler was the forefather of both the new germanium element and also the chemistry of its organic derivatives, whereas Mendeleev was their Nostradamus.

During the period between 1887 and 1925 no new organogermanium compound was reported. The forty years of the dry season resulted mainly from the scarcity and high prices of germanium and its simplest inorganic derivatives. This reflected the low natural reserves of argirodit, the only mineral source of germanium known at that time. The picture changed dramatically when in 1922 new sources of germanium were discovered. In particular, 0.1–0.2% of Ge were found in a residue of American zinc ore after zinc removal^{139,140}. Dennis developed a method for the isolation of tetrachlorogermane from the ore¹⁴¹. In 1924, 5.1% of Ge was found in germanite, a mineral from southwestern Africa. Renhierite, a mineral from the Belgian Congo, containing 6–8% of Ge¹⁴², became another source of germanium. In 1930–1940, processing wastes of coal ashes and sulfide ores became the main sources of germanium^{34,141,143,144}. These developments allowed American, English and German chemists to start in 1925 to carry

out fundamental investigations of organogermanium compounds, in spite of the fact that germanium was still very expensive^{145–150}.

Thus, the chemistry of organogermanium compounds actually started to develop in the second quarter of the twentieth century. Its founders were L. M. Dennis, C. A. Kraus, R. Schwartz and H. Bayer, whose results were published in 1925–1936. A period of low activity then followed in this field and was resumed only in the middle of the century by leaders such as E. Rochow, H. Gilman, H. H. Anderson, O. H. Johnson, R. West and D. Seyferth. Organogermanium chemistry started to flourish in the sixties when many new investigators joined the field. These included the French chemists M. Lesbre, J. Satge and P. Mazerolles, the German chemists M. Schmidt, H. Schmidbaur, M. Wieber, H. Schumann and J. Ruidisch, the English chemists F. Glockling and C. Eaborn, the Russian chemists V. F. Mironov, T. K. Gar, A. D. Petrov, V. A. Ponomarenko, O. M. Nefedov, S. P. Kolesnikov, G. A. Razuvaev, M. G. Voronkov and N. S. Vyazankin, the Dutch chemist F. Rijkens the American chemist J. S. Thayer and others.

Activity was stimulated by the intensive development of the chemistry of organometallic compounds, particularly of the silicon and tin derivatives. The chemistry of organogermanes was significantly developed as well due to the essential role of germanium itself and its organic derivatives in electronics^{151,152}, together with the discovery of their biological activities (including anticancer, hypotensive, immunomodulating and other kinds of physiological action)^{80,81,86,153}. In addition, a progressive decrease in the prices of elemental germanium and its derivatives expanded their production and helped their growth. The rapid expansion of organogermanium chemistry is clearly evident due to the increase in the number of publications in this field.

From 1888 till 1924 there were no publications and prior to 1934 just 26 publications were devoted to organogermanes¹⁵⁴. Only 25 references on organogermanium compounds were listed in an excellent monograph by Krause and Grosse published in 1937¹⁵⁵; 60 publications appeared before 1947¹⁵⁶, 99 before 1950¹⁵⁷ and 237 during the period 1950–1960^{48,78}. By 1967 the number of publications was over 1800 and by 1971 it exceeded 3000^{36,37}. By 1970 about 100 publications had appeared annually^{36,79} and by this time 370 reviews dealing with organogermanium compounds had appeared⁷⁹.

In 1951 already 230 organogermanium compounds were known¹⁵⁷, in 1961 there were 260¹⁵⁸ and in 1963 there were more than 700¹⁵⁹.

As the chemistry of organogermanium compounds is three-quarters of a century younger than the organic chemistry of tin and lead, it is reasonable to consider in this chapter the most important references published before 1967, when two classical monographs were published^{36,37,78}. Due to space limitation we will avoid, where possible, citing reaction equations in the hope that they will be clear to the readers.

B. Organometallic Approaches to a C–Ge and Ge–Ge Bond

Thirty-eight years after Winkler developed the organozinc method for the synthesis of tetraethylgermane, Dennis and Hance¹⁶⁰ reproduced it, but this method for synthesis of aliphatic germanium derivative was not used later. However, in the years 1927–1935 arylzinc halides were used for the synthesis of tetraarylgermanes^{23,161–165}.

Application of Grignard reagents in organometallic synthesis led to the synthesis of common aliphatic, aromatic and alicyclic germanium derivatives during the years 1925–1932. Dennis and Hance¹⁶⁰ were the first to produce in 1925 tetraalkylgermanes R_4Ge ($R = Me, Et, Pr, Bu, Am$)^{145,160,166–169} from Grignard reagents. Kraus and Flood¹⁴⁸ used organomagnesium reagents for the synthesis of tetraalkylgermanes. In 1925 Morgan and Drew¹⁴⁹, and later Kraus and Foster¹⁶¹ synthesized tetraphenylgermane, the

first compound having a Ph–Ge bond, from GeCl_4 and PhMgBr . The maximum (70–75%) yield was reached at a $\text{GeCl}_4 : \text{PhMgBr}$ ratio of 1 : 5^{170,171}.

In 1934 Bauer and Burschkies¹⁷², and only later other researchers^{173–176} showed for the first time that a reaction of GeCl_4 and Grignard reagents results in hexaorganoyldigermanes R_3GeGeR_3 ($\text{R} = 4\text{-MeC}_6\text{H}_4$ and PhCH_2). In 1950, Johnson and Harris¹⁷³ noted the formation of hexaphenyldigermane in the reaction of GeCl_4 with an excess of PhMgBr . Glockling and Hooton^{177,178} later found that if the above reaction was carried out in the presence of magnesium metal, hexaphenyldigermane $\text{Ph}_3\text{GeGePh}_3$ was produced in a higher yield along with Ph_4Ge . Seyferth¹⁷⁶ and Glockling and Hooton¹⁷⁸ concluded that the intermediate product in the reaction of GeCl_4 and ArMgBr leading to $\text{Ar}_3\text{GeGeAr}_3$ was Ar_3GeMgBr .

In line with this assumption Gilman and Zeuech¹⁷⁹ found in 1961 that Ph_3GeH reacted with several Grignard reagents (such as $\text{CH}_2=\text{CHCH}_2\text{MgX}$ or ArMgBr) to give Ph_3GeMgX ($\text{X} = \text{Cl}, \text{Br}$). The latter has cleaved THF, since a product of the reaction followed by hydrolysis seemed to be $\text{Ph}_3\text{Ge}(\text{CH}_2)_4\text{OH}$. Mendelsohn and coworkers¹⁸⁰ indicated the possibility of the formation of R_3GeMgX in the reaction of GeCl_4 and Grignard reagents.

In the period 1931–1950 the organomagnesium syntheses became the laboratory practice for preparing tetraorganoylgermanes.

Tetraalkyl- and tetraarylgermanes containing bulky organic substituents could be synthesized only with difficulty, if at all, using Grignard reagents. In this case the reaction resulted in triorganoylhalogermane^{181–183}.

Organoylhalogermanes $\text{R}_{4-n}\text{GeX}_n$ ($n = 1\text{--}3$) were prepared for the first time in 1925 by Morgan and Drew¹⁴⁹, who isolated phenylbromogermanes $\text{Ph}_{4-n}\text{GeBr}_n$ ($n = 1, 3$) together with tetraphenyldigermane from the reaction of GeBr_4 and PhMgBr . However, the organomagnesium synthesis of organoylhalogermanes has not found much use due to the simultaneous production of other compounds and the difficulty of separating them. The only exceptions were R_3GeX products having bulky R substituents^{172,181,183,184}.

In the reaction of HGeCl_3 and MeMgBr , Nefedov and Kolesnikov¹⁸⁵ obtained a mixture of both liquid and solid permethyloligogermanes $\text{Me}(\text{Me}_2\text{Ge})_n\text{Me}$.

In 1932, Krause and Renwanz¹⁸⁶ synthesized the first heterocyclic organogermanium compound, tetra-2-thienylgermane, from the corresponding Grignard reagent. In the same year Schwarz and Reinhardt¹⁵⁰ synthesized by the same method the first germacycloalkanes (1,1-dichloro- and 1,1-diethyl-1-germacyclohexanes). They also synthesized tetra-*N*-pyrrolylgermane by the reaction of GeCl_4 and potassium pyrrole.

Since 1926 the organomagnesium synthesis was also used for preparing more complex tetraorganoylgermanes^{145,162,163,169,172,187–190} such as $\text{R}_3\text{GeR}'$, $\text{R}_2\text{GeR}'_2$ and $\text{R}_2\text{GeR}'\text{R}''$.

The first unsaturated organogermanium compounds having α,β - or β,γ -alkynyl groups at the Ge atom were synthesized in 1956–1957 by Petrov, Mironov and Dolgy^{191,192} and by Seyferth^{176,193,194} using Grignard or Norman reagents.

In 1925, the Dennis group used along with the organozinc and organomagnesium synthesis of tetraorganoylgermanes, also the Wurtz–Fittig reaction (i.e. the reaction of aryl halides with sodium metal and tetrahalogermanes^{168,187,195}). The Wurtz–Fittig reaction was extensively employed for the synthesis of organogermanium compounds having Ge–Ge bonds such as R_3GeGeR_3 . The first representative of the $\text{Ph}_3\text{GeGePh}_3$ series was synthesized in 1925 by Morgan and Drew¹⁴⁹, and subsequently by Kraus and coworkers^{161,196}, using the reaction of triphenylbromogermane and sodium metal in boiling xylene. Analogously, Bauer and Burschkies¹⁷² produced in 1934 R_3GeGeR_3 , $\text{R} = 4\text{-MeC}_6\text{H}_4$ and PhCH_2 . In addition, they found that the reaction of GeCl_4 , Na and RBr ($\text{R} = 4\text{-MeC}_6\text{H}_4$) led to R_3GeGeR_3 in good yield together with R_4Ge . In 1932,

Kraus and Flood¹⁴⁸ found that hexaethyldigermene was not formed in the reaction of triethylbromogermene and sodium metal in boiling xylene. However, they produced hexaethyldigermene by heating Et_3GeBr and Na in a sealed tube at 210–270 °C without solvent or by the reaction of Et_3GeBr and Na in liquid ammonia.

The possibility of producing diphenylgermylene alkali metal derivatives like Ph_2GeM_2 ($\text{M} = \text{Li}, \text{Na}$) was shown in 1952 by Smyth and Kraus¹⁹⁷ when they obtained Ph_2GeNa_2 by cleavage of Ph_4Ge with concentrated solution of sodium in liquid ammonia. In 1930, Kraus and Brown¹⁹⁸ produced a mixture of perphenyloligocyclogermanes $(\text{Ph}_2\text{Ge})_n$ by the reaction of sodium metal with diphenyldichlorogermene in boiling xylene. However, only in 1963 did Neumann and Kühle¹⁹⁹ show that the main crystalline product of the reaction is octaphenylcyclotetragermene $(\text{Ph}_2\text{Ge})_4$. Cleavage of $(\text{Ph}_2\text{Ge})_n$ with sodium in liquid ammonia resulted in Ph_2GeNa_2 . Reaction of $(\text{Ph}_2\text{Ge})_4$ with iodine which resulted in cleavage of the Ge–Ge bond, allowed the authors¹⁹⁹ to synthesize the first organotetragermenes involving three Ge–Ge bonds $\text{X}[\text{Ph}_2\text{Ge}]_4\text{X}$ ($\text{X} = \text{I}, \text{Me}, \text{Ph}$). By the reaction of diphenyldichlorogermene and lithium (or sodium naphthalene) Neumann and Kühle^{175,199,200} isolated higher perphenylcyclogermanes with $n = 5$ (37%) and $n = 6$ (17%). It is particularly remarkable that, unlike their homologs with $n = 4$, these compounds could not be cleaved with iodine.

In 1962–1965 Nefedov, Kolesnikov and coworkers^{201–205} investigated the reaction of Me_2GeCl_2 with lithium metal in THF. The main products were $(\text{Me}_2\text{Ge})_6$ (80% yield) at 20–45 °C and the polymer $(\text{Me}_2\text{Ge})_n$ (50% yield) at 0 °C.

In 1966 Shorygin, Nefedov, Kolesnikov and coworkers²⁰⁶ were the first to investigate and interpret the UV spectra of permethyloligogermenes $\text{Me}(\text{Me}_2\text{Ge})_n\text{Me}$ ($n = 1–5$). The reaction of Et_2GeCl_2 with Li in THF led mostly to polydiethylgermane $(\text{Et}_2\text{Ge})_n$ ²⁰⁷. At the same time Mironov and coworkers^{208,209} obtained dodecamethylcyclohexagermane $(\text{Me}_2\text{Ge})_6$ by the same procedure.

In 1969, Bulten and Noltes²¹⁰ synthesized the perethyloligogermenes $\text{Et}(\text{Et}_2\text{Ge})_n\text{Et}$ ($n = 2–6$) by the organolithium method. The oligomer with $n = 6$ was thermally stable and heating at 250 °C for 8 hours resulted in only 20% decomposition.

By a reaction of Li amalgam with Ph_2GeBr_2 , Metlesics and Zeiss²¹¹ produced 1,2-dibromotetraphenyldigermene instead of the cyclic oligomers obtained previously in a similar reaction with Li metal. A reaction of Li amalgam with PhGeBr_3 gave $\text{PhBr}_2\text{GeGeBr}_2\text{Ph}$, the thermolysis of which resulted in PhGeBr_3 .

Curiously, the reaction of phenyltrichlorogermene with sodium or potassium produced a compound $(\text{PhGe})_n$, which Schwarz and Lewinsohn¹⁸⁷ mistook for hexaphenylhexagermabenzene Ph_6Ge_6 . Five years later Schwartz and Schmeisser²¹² found that the action of potassium metal on PhGeCl_3 yielded a product, assigned by them to be a linear hexamer having terminal Ge(III) atoms i.e. a biradical of a structure $\cdot(\text{PhGe}=\text{GePh})\cdot$. They thought that this structure could be confirmed by addition reactions with bromine, iodine and oxygen, which indeed took place. However, HI and HBr were not involved in the addition reactions.

Two dozen years later Metlesics and Zeiss²¹³ obtained the same product by the reaction of PhGeCl_3 with Li amalgam. They found that the product was a polymer consisting of $(\text{PhGe})_n$, $(\text{Ph}_2\text{Ge})_n$ and $(\text{PhGeO})_n$ chains.

In 1950–1960 it was found that triarylgermyl derivatives of alkali metals could be obtained by cleavage of $\text{Ge}-\text{H}^{214,215}$, $\text{C}-\text{Ge}^{174,195,216,217}$, $\text{Ge}-\text{Ge}^{218–221}$ and $\text{Ge}-\text{Hal}^{222}$ bonds by Li, Na or K in the appropriate solvents.

In 1950, Glarum and Kraus²¹⁴ investigated the reaction of alkylgermanes $\text{R}_{4-n}\text{GeH}_n$ ($n = 1–3$) and sodium metal in liquid ammonia. They found that alkylgermanes RGeH_3 reacted with Na to give RGeH_2Na .

As early as in 1927, Kraus and Foster¹⁶¹ produced for the first time triphenylgermylsodium as its ammonia complex $\text{Ph}_3\text{Ge}(\text{NH}_3)_3\text{Na}$. They also found that the reaction of Ph_3GeNa with H_2O or NH_4Br in liquid ammonia led quantitatively to Ph_3GeH . The reaction of Ph_3GeNa and Ph_3GeF in liquid ammonia resulted in $\text{Ph}_3\text{GeGePh}_3$.

In 1957–1959, Gilman and coworkers^{220,222} found that $\text{Ph}_3\text{GeGePh}_3$ was cleaved by sodium in THF solution in the presence of PhBr and Ph_4Ge to give Ph_3GeNa .

In 1932 it was found that the reaction of Ph_3GeNa with organic halides RX gave Ph_3GeR ¹⁹⁶, whereas when $\text{R} = \text{Ph}$, Ph_3Ge ^{196,198,223,224} was isolated. The reaction of Ph_3GeNa with oxygen led to Ph_3GeONa ¹⁶¹. In the years 1950–1952, Kraus and coworkers further developed this chemistry by studying the reactions of Ph_3GeNa with organic mono- and dihalides of different structure, such as HCCl_3 , CCl_4 ¹⁹⁷, BCl_3 ²²⁴ or HSiCl_3 ²²⁵. The product of the latter reaction was $(\text{Ph}_3\text{Ge})_3\text{SiH}$.

In 1930, Kraus and Brown^{198,226} prepared octaphenyltrigermane by the reaction of Ph_3GeNa and Ph_2GeCl_2 . It was the first organogermanium compound with more than one Ge–Ge bond. The two Ge–Ge bonds could readily be cleaved by bromine. Kraus and Scherman²²⁴ synthesized in 1933 the first unsymmetrical hexaorganodigermane $\text{Ph}_3\text{GeGeEt}_3$ by the reaction of Ph_3GeNa and Et_3GeBr .

In 1932, Kraus and Flood¹⁴⁸ prepared the first compound having a Ge–Sn bond ($\text{Ph}_3\text{GeSnMe}_3$) by the reaction of Ph_3GeNa and Me_3SnBr . In 1934, Kraus and Nelson²²⁷ synthesized $\text{Ph}_3\text{GeSiEt}_3$ by the reaction of Ph_3GeNa and Et_3SiBr .

The reaction of hexaethyldigermane and potassium in ethylamine solution led Kraus and Flood¹⁴⁸ to the first synthesis of triethylgermylpotassium. Its reaction with ethyl bromide resulted in Et_4Ge . However, attempts to cleave hexamethyldigermane either by potassium or by its alloy with sodium were unsuccessful²²⁸.

The action of potassium metal with Me_3GeBr without solvent resulted in $\text{Me}_3\text{GeGeMe}_3$ ²²⁸. Gilman and coworkers^{217–220,229} synthesized Ph_3GeK by cleavage of $\text{Ph}_3\text{GeGePh}_3$ with a sodium and potassium alloy in THF in the presence of an initiator (PhBr or Ph_4Ge). Triphenylgermylpotassium was produced in a 26% yield during a slow cleavage of $\text{Ph}_3\text{CGePh}_3$ by the same alloy¹⁹⁵. The development of a method for the synthesis of Ph_3GeK opened a route to carry out its addition to double bonds, such as 1,1-diphenylethylene, which resulted in $\text{Ph}_2\text{CH}_2\text{CH}_2\text{GePh}_3$ ²²⁰, or to activated conjugated bonds²²⁰.

Lithium metal has been used for organogermanium synthesis since 1932, but organolithium compounds were used only since 1949^{173,230}. Lithium and its organic derivatives were used in three approaches: (1) reactions of lithium and organogermanium compounds; (2) reactions of organolithium compounds with organic and inorganic germanium compounds; (3) synthesis based on compounds having a Ge–Li bond.

Although fundamental research in this field was undertaken in Gilman's laboratory, Kraus and Flood¹⁴⁸ were the pioneers in using lithium for the synthesis of organogermanium compounds. In 1932, they discovered that the reaction of Et_3GeX ($\text{X} = \text{Cl}, \text{Br}$) and lithium in ethylamine resulted in $\text{Et}_3\text{GeGeEt}_3$. With excess lithium, the Ge–Ge bond of hexaethyldigermane was cleaved to give Et_3GeLi . When the latter was treated with NH_3 or NH_4Br in an ethylamine solution, Et_3GeH was formed.

In 1950, Glarum and Kraus²¹⁴ developed a very convenient method for the synthesis of alkylgermyllithium compounds (RGeH_2Li) by the reaction of RGeH_3 with lithium in ethylamine solution. An analogous reaction of R_2GeH_2 and lithium led to R_2GeHLi . Later, Vyazankin, Razuvaev and coworkers^{231–234} synthesized Et_3GeLi in >90% yield by the reaction of lithium and $(\text{Et}_3\text{Ge})_2\text{Hg}$ or $(\text{Et}_3\text{Ge})_2\text{Ti}$.

Gilman and coworkers^{216,222} obtained Ph_3GeLi by a simpler method. The reaction of Ph_3GeBr with Li in THF gave the compound, although in a lower (52%) yield. In 1956,

Gilman and Gerow^{229,235} synthesized Ph_3GeLi in 70% yield by the cleavage of Ph_4Ge with lithium metal in a diglyme solution. They later showed that aryl groups were cleaved from the Ge atom in the same solvent much more easily than alkyl or phenyl groups.

Tamborski and coworkers²³⁶ found that the reaction of Ph_3GeCl and lithium metal in THF involved the intermediate formation of $\text{Ph}_3\text{GeGePh}_3$ and resulted in Ph_3GeLi .

Gross and Glockling²³⁷ developed in 1964 a very effective method for the synthesis of $(\text{Ph}_2\text{CH}_2)_3\text{GeLi}$ based on the cleavage of $(\text{PhCH}_2)_4\text{Ge}$ by lithium in diglyme. Gross and Glockling^{237,238} found that, when tetrabenzylgermane is treated with lithium, two PhCH_2 groups were cleaved, and $(\text{PhCH}_2)_2\text{GeLi}_2$ was probably formed.

The organolithium synthesis proved to be the simplest and most convenient route to organogermanium compounds, including those carrying bulky substitutes on the Ge atom. The method was first used in 1930 by Kraus and Brown¹⁹⁸ and found many applications shortly after.

In 1949, Johnson and Nebergall²³⁰ showed that the use of RLi for R_4Ge production resulted in higher yields than that for RMgX . Ten years later Gilman and coworkers¹⁷⁴ found that the reaction of GeBr_4 and EtLi led to Et_4Ge and $\text{Et}_3\text{GeGeEt}_3$. In 1953, Summers²³⁹ discovered that reaction of PhLi with GeI_2 gave a polymer $(\text{Ph}_2\text{Ge})_n$. In contrast, the reaction of GeI_2 with Bu_2Hg produced 1,2-diiodotetrabutylidigermane²⁴⁰.

Developed by Nefedov, Kolesnikov and coworkers^{185,203}, the reaction of RLi with HGeCl_3 resulted in linear and cyclic oligomers and polymers consisting of alternate Ge—Ge bonds.

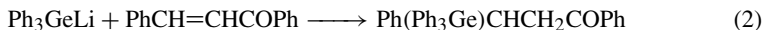
The Ge—H bonds in triarylgermanes were cleaved as well by organolithium compounds to form Ar_3GeLi ²³⁵. Together with the latter Ar_3GeR and $\text{Ar}_3\text{GeGeAr}_3$ were also formed^{173,235}. Johnson and Harris¹⁷³ investigated the reaction of PhLi and Ph_3GeH and found that, depending on the mixing sequence of the reagents, the product could be either Ph_4Ge or $\text{Ph}_3\text{GeGePh}_3$. Trialkylgermanes reacted less readily than triarylgermanes with RLi ($\text{R} = \text{Bu}, \text{Ph}$)²⁴¹.

In 1956, Gilman and Gerow^{229,235} and then Brook and Peddle²⁴² developed an effective, nearly quantitative method for the synthesis of Ph_3GeLi by the reaction of Ph_3GeH and BuLi .

Gilman and coworkers^{220,229,235,243} found that Ph_3GeLi could be added to 1,1-diphenylethylene, 1-octadecene and benzalacetophenone (but not to 1-octene, cyclohexene and E-stilbene). The reaction of Ph_3GeLi with enolizable ketones followed equation 1²⁴⁴.



On the other hand, addition of Ph_3GeLi to benzophenone gave $\text{Ph}_2(\text{Ph}_3\text{Ge})\text{COH}$ ²⁴⁴. An analogous addition of Ph_3GeLi to formaldehyde and benzaldehyde led to $\text{Ph}_3\text{GeCH}_2\text{OH}$ ²⁴⁴ and $\text{Ph}(\text{Ph}_3\text{Ge})\text{CHOH}$ ^{242,245}, respectively. Triphenylgermyllithium adds to 1,4-benzalacetone (equation 2)²¹⁸ and reacts as a metal-active reagent with CH acids such as fluorene^{195,246}.



Chalcogens E ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$) readily insert into the Ge—Li bond. For example, reaction of E with PhGeLi yields Ph_3GeELi ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$)²⁴⁷. Brook and Gilman found that triphenylgermyllithium was oxidized to Ph_3GeOLi , and carbon dioxide could easily be inserted into the molecule to give $\text{Ph}_3\text{GeCOOLi}$ ²³⁵. Thermal decomposition of Ph_3GeCOOH led to Ph_3GeOH ¹⁹⁵. Triphenylgermyllithium cleaved the oxirane ring with ring opening to give $\text{Ph}_3\text{GeCH}_2\text{CH}_2\text{OLi}$ ²⁴⁸.

The reactions of GeI_2 with organic lithium, manganese, aluminum and mercury derivatives^{185,201,239,240,249} were widely investigated as a possible route for producing diorganylgermylene R_2Ge . However, the reaction proceeds in a complex manner and has no preparative application. However, Glockling and Hooton²⁴⁹ discovered later that the reactions of GeI_2 and phenyllithium or mesitylmagnesium bromide led to the corresponding products Ar_3GeLi or Ar_3GeMgBr whose hydrolysis resulted in Ar_3GeH . The first bulky oligogermane, i.e. $(\text{Ph}_3\text{Ge})_3\text{GeH}$, was obtained in 1963 by this reaction²⁴⁹. A year later Vyazankin and coworkers²⁵⁰ synthesized methyl-tris(triphenylgermyl)germane $(\text{Ph}_3\text{Ge})_3\text{GeMe}$.

C. Nonorganometallic Approaches to a C—Ge Bond

E. G. Rochow, whose name became famous due to his discovery of the direct synthesis of organohalosilanes from elementary silicon^{2,4,5}, tried to develop an analogous method for the synthesis of organohalogermanes. In 1947 he showed that the methylhalogermanes MeGeX_3 and Me_2GeX_2 were formed in the reaction of methyl chloride or methyl bromide and elementary germanium in the presence of copper or silver metals at $300\text{--}400^\circ\text{C}$ ²¹³. Later, he added EtCl , PrCl and PhCl ^{251–255} to the reaction. Generally, a mixture of alkylhalogermanes $\text{R}_{4-n}\text{GeX}_n$ ($n = 2, 3$) was obtained in the process. The product ratios were dependent on the temperature and the catalyst structure. When MeCl and EtCl were used a mixture of R_2GeCl_2 and RGeCl_3 , $\text{R} = \text{Me, Et}$, was formed in a ratio very close to 2 : 1. The yields of methyltrichlorogermane were increased on increasing the temperature and were dependent on the copper content in the contact mass, as well as on the addition of Sb , As and ZnCl_2 ^{66,191,256} to the reaction mixture.

In 1956–1958, this direct organylhalogermanes synthesis was thoroughly investigated at the Petrov, Mironov and Ponomarenko laboratory^{66,191,257,258}. A variety of halides, such as allyl and methallyl chloride, allyl bromide²⁵⁸ and CH_2Cl_2 ²⁵⁹ (but, not vinyl chloride), were found to react. With the latter, MeGeCl_3 (27%), $\text{Cl}_3\text{GeCH}_2\text{GeCl}_3$ (23%) and $(\text{CH}_2\text{GeCl}_2)_3$ (19%) were produced. Alkyltribromogermanes RGeBr_3 ($\text{R} = \text{Pr, Bu}$) were synthesized by the reaction of the corresponding alkyl bromides with sponged germanium at $300\text{--}340^\circ\text{C}$.

Alkylidogermanes were produced by direct synthesis only in 1963–1966^{260–264}. It is noteworthy that no compounds having Ge—H bonds (such as RGeHCl_2 or R_2GeHCl) were formed during the direct synthesis of alkylchlorogermanes, in contrast with the direct synthesis of alkylchlorosilanes.

A hydrogermylation reaction (the term was first introduced by Lukevics and Voronkov^{52,53,77}, i.e. the addition of organic and inorganic germanium derivatives having Ge—H bonds to unsaturated compounds) was first performed by Fischer, West and Rochow²⁶⁵ in 1954. They isolated hexyltrichlorogermane (in 22% yield) after refluxing for 35 hours a mixture of trichlorogermane and 1-hexene in the presence of a benzoyl peroxide initiator. Two years later, the reaction of HGeCl_3 and other alkenes in the presence of the same initiator was carried out at $70\text{--}85^\circ\text{C}$ to give the appropriate alkyltrichlorogermanes in low yields (9–24%)²⁶⁶ as well. In 1957, Gilman and coworkers added HGeCl_3 to 1-octene²⁶⁷, 1-octadecene²¹⁷, cyclohexene²⁶⁷, allyltriphenylsilane²⁶⁸ and -germane²¹⁷ in the presence of benzoyl peroxide or under UV radiation.

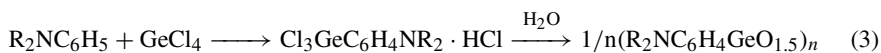
In 1958 Ponomarenko and coworkers²⁶⁹ found that HGeCl_3 was exothermally added to ethylene at 40 atm pressure in the presence of H_2PtCl_6 to give EtGeCl_3 in 25% yield. In the same year Mironov and Dzhurinskaya in Petrov's laboratory unexpectedly discovered that the reaction of HGeCl_3 and diverse unsaturated compounds proceeded exothermally at room temperature and without either catalyst or initiator^{270–272}. On the

contrary, the presence of either a catalyst or an initiator actually decreased the yield of the hydrogermylation products^{270–272}.

A noncatalytic hydrogermylation reaction was carried out at 85 °C in a sealed tube in 1956²⁶⁶. Furthermore, HGeBr₃²⁷³, HGeI₃²⁷⁴, R₂GeHCl (at 100–150 °C)²⁷⁵, R₂GeHBr (at 150 °C)²⁷⁵, R₂GeH₂ (at 140–150 °C)²⁷⁶ and R₃GeH (at 50–200 °C)^{276–278} were reacted in the noncatalytic hydrogermylation process. However, addition of R₃GeH to unsaturated compounds proceeded more easily in the presence of H₂PtCl₆^{52,53}.

In 1962, Satge and Lesbre^{279,280} carried out for the first time hydrogermylation of the carbonyl group of aldehydes and ketones.

The best method for the synthesis of aryltrihalogermanes based on the reaction of aryl iodides and GeX₄ (X = Cl, Br) in the presence of copper powder was discovered by Mironov and Fedotov^{281,282} in 1964. Bauer and Burschkies¹⁸¹ discovered in 1932 an unusual way of Ge–C bond formation by condensation of GeCl₄ and aromatic amines according to equation 3. The reaction products were isolated as the corresponding substituted phenylgermsesquioxanes.



In 1955, Seyferth and Rochow²⁸³ developed a nontrivial method of Ge–Ge bond formation based on the insertion of a carbene (H₂C: formed from diazomethane) into a Ge–Cl bond of GeCl₄ to form ClCH₂GeCl₃. Later, Seyferth and coworkers^{284,285} extended this approach to the formation of the GeCH₂X (X = Cl, Br) group by the reaction of dihalocarbenes (generated from PhHgCX₂Br) with Ge–H bonds.

Kramer and Wright^{286,287} and Satge and Rivi  re²⁸⁸ demonstrated the possibility of carbene (formed from diazomethane) insertion into the Ge–H bond to give a Ge–CH₃ moiety. However, this reaction is of no practical application. It was more interesting to insert substituted carbenes (generated from diazo derivatives such as ethyl diazoacetate, diazoacetone and diazoacetophenone) into Ge–H bonds in the presence of copper powder. In this case a Ge–CH₂X group was formed, where X was the corresponding functional group^{276,277,289}.

In 1958, Nesmeyanov and coworkers²⁹⁰ found that decomposition of aryl diazonium tetrafluoroborates with zinc dust in the presence of GeCl₄ resulted in formation of aryltrichlorogermanes in <30% yield, isolated as the corresponding arylgermsesquioxanes.

In 1960, Volpin, Kursanov and coworkers^{291–293} showed that dihalogermynes add to multiple bonds by reacting GeI₂ with tolan (PhC≡CPh) at 220–230 °C²⁹². The main product of the reaction was assigned to 1,1-diiodo-2,3-diphenyl-1-germa-2-cyclopropene, which the authors considered to be a new three-membered heterocyclic aromatic system^{291,292,294}. When this substance was allowed to react with RMgX (R = Me, Et), the iodine atoms were replaced by alkyl substituents, whereas upon the action of NaOH they were substituted by OH groups. The OH groups of the hydroxy derivative obtained were replaced by halogen²⁹¹ on reaction with HCl or HBr. However, it was established later that the isolated adduct was actually 1,1,4,4-tetraiodo-2,3,5,6-tetraphenyl-1,4-digerma-2,5-cyclohexadiene^{295–298}.

Reaction of GeI₂ and acetylene at 130–140 °C and 10 atm²⁹⁹ gave 44% yield of an adduct whose structure was assigned to 1,1-diiodo-1-germa-2-cyclopropene (i.e. 1,1-diiododigermylene)²⁹⁹. Its iodine atoms were replaced by OH and Cl atoms²⁹⁹ and by Me groups using known reactions. However, X-ray analysis established the structure of the isolated chlorinated compound as 1,1,4,4-tetrachloro-1,4-digerma-2,5-cyclohexadiene. Hydrogenation of 1,1,4,4-tetramethyl derivative synthesized from the latter afforded the 1,1,4,4-tetramethyl-1,4-digermacyclohexane, whereas its bromination

led to $\text{Me}_2\text{Ge}(\text{CH}=\text{CHBr})\text{Br}$ ²⁹⁷. Simultaneously, a polymer $(-\text{I}_2\text{Ge}-\text{CH}=\text{CH}-)_n$ ²⁹⁹ with average molecular weight of 4300 (after removal of lower molecular weight fractions) was formed in a 56% yield. Probably the low molecular weight polymer fractions had macrocyclic structures resembling their silicon analog $(-\text{R}_2\text{SiCH}=\text{CH}-)_n$ ³⁰⁰. The reaction of acetylene with GeBr_2 leads to analogous polymers.

In 1960, Russian chemists found that GeI_2 acts easily with diarylmercuranes Ar_2Hg to give $\text{Ar}_{4-n}\text{GeI}_n$ ($n = 1, 2$) in good yield³⁰¹, together with ArHgI and Hg . In contrast, dialkyl mercury derivatives reduced GeI_2 to Ge metal, but did not form dialkyldiiodogermanes (one of the products was $\text{I}_2\text{RGeGeRI}_2$)²⁴⁰.

In 1963, Mironov and Gar³⁰² showed that GeCl_2 and GeBr_2 ^{273,303} (generated from HGeX_3) add to 1,3-butadiene to give the corresponding 1,1-dihalo-1-germa-3-cyclopentene. Analogously^{304,305}, GeI_2 adds to 2-methyl- and 2,3-dimethylbutadiene.

Another approach to the formation of a C–Ge bond resulting in organyltrihalogermanes was based on the reaction of dihalogermynes (GeX_2) with organic halides. For this purpose, the more stable and easily available GeI_2 was usually used. In 1933, Flood and coworkers^{306,307} discovered that the reaction of GeI_2 with alkyl iodides proceeds smoothly to give alkyltriiodogermanes. Pope³⁰⁸ and Pfeiffer³⁰⁹ and their coworkers performed analogous synthesis of RSnI_3 from SnI_2 as early as 1903. This reaction can be regarded as an insertion of diiodogermylene into the C–I bond. F_3GeGeI_3 ³¹⁰, ICH_2GeI_3 , PhGeI_3 , $\text{MeOCH}_2\text{GeI}_3$ and $\text{EtOCH}_2\text{GeI}_3$ were also similarly synthesized at 110–290 °C in sealed ampoules.

In 1965, Mironov and Gar^{273,303} found that allyl bromide adds easily to GeBr_2 to form allyltribromogermane in a 65% yield. In 1935, Tchakirian and Lewinsohn³¹¹ used a complex of GeCl_2 and CsCl , i.e. cesium trichlorogermane (CsGeCl_3), to synthesize RGeCl_3 . Heating CsGeCl_3 with PhI at 250 °C afforded phenyltrichlorogermane in 80% yield. Alkyl iodides also reacted similarly under similar conditions^{312,313}. However, this method did not find any application.

D. C–Ge Bond Cleavage. Organylhalogermanes

The C–Ge bond is less stable toward heterolytic and homolytic cleavage reactions than the C–Si bond, but it is more stable than the C–Sn and C–Pb bonds. This is consistent with the bond energies of these bonds (see Chapter 2).

The first example of heterolytic cleavage of the C–Ge bond was the cleavage of tetraorganylgermanes (and later of organylhalogermanes) by halogens or hydrogen halides (mainly Br_2 and HBr). A synthetic method of organylhalogermanes ($\text{R}_{4-n}\text{GeX}_n$, $n = 1-3$) based on this reaction has been widely used. It was first used in 1927 in the laboratories of Kraus¹⁶¹ and Dennis¹⁴⁵ and afterwards by many chemists^{162,163,165,172,173,187,314}.

In 1927, Kraus and Foster¹⁶¹ showed that refluxing tetraphenylgermane with a bromine solution in CCl_4 for 7 hours gave triphenylbromogermane. In the same year, Orndorff, Tabern and Dennis¹⁴⁵ discovered that by using 1,2-dibromoethane as a solvent, the reaction was completed within a few minutes. The second phenyl group could be also cleaved, but with difficulty. However, with excess bromine, or by adding AlBr_3 , catalyst more Ar_2GeBr_2 was obtained in satisfactory yields. In 1931, Schwarz and Lewinsohn¹⁸⁷ cleaved the Ar–Ge bond in many tetraarylgermanes by bromine.

In 1932, Kraus and Flood¹⁴⁸ obtained Et_3GeBr in 82% yield during bromination of tetraethylgermanium in an EtBr media. R_3GeBr derivatives ($\text{R} = \text{Pr}$ ³¹⁵, Bu ^{314,316}) were then synthesized by the same method. The feasibility of cleavage of substituents attached to the Ge atom by reaction with bromine decreases in the following order: $4\text{-PhC}_6\text{H}_4 > \text{Ph} > \text{CH}_2=\text{CHCH}_2 > \text{Bu} > i\text{-Pr} > \text{Pr} > \text{Et} > \text{Me}$ ⁷⁷.

In the early 1950s Anderson^{315,317} used bromine, or bromine and iodine halides in the presence of iron powder (i.e. FeX_3 formed *in situ*) to cleave the C–Ge bond.

In a number of cases, cleavage of R_4Ge with bromine gave mixtures of $\text{R}_{4-n}\text{GeBr}_n$ ($n = 1-3$) which were difficult to separate. Fuchs and Gilman³¹⁸ suggested separating such mixtures by hydrolysis to the corresponding oxygen derivatives followed by their retransformation to halides. Organyliodogermanes were obtained by C–Ge bond cleavage with iodine and AlI_3 catalyst. EtGeI_3 was obtained from Et_2GeI_2 by this method³¹⁹.

Organyliodogermanes and organylfluorogermanes were prepared by the reaction of isostructural organylhalogermanes (chlorides and bromides) with NaI in acetone or with SbF_3 ¹⁸⁴, respectively.

In 1930, Dennis and Patnode¹⁶⁷ used HBr for the first time to cleave the C–Ge bond. In each case, the reaction did not continue beyond the stage of forming R_3GeBr ^{162,163,167,320}. By this approach, they obtained Me_3GeBr from Me_4Ge . Five years later Simons¹⁶³ showed that the rate of the C–Ge bond cleavage by HBr decreased in the following order of the Ge substituents: $4\text{-MeC}_6\text{H}_4 > 3\text{-MeC}_6\text{H}_4 > \text{Ph} > \text{PhCH}_2$.

R_4Ge ($\text{R} = \text{Me}, \text{Et}$) cleavage by HF was carried out by Gladstein and coworkers³²¹ in 1959. R_4Ge reacted with HCl or HI only in the presence of aluminum halides³²².

It is noteworthy that under the action of sulfuric acid the C–Ge bond of $(\text{PhCH}_2)_4\text{Ge}$, was not cleaved, and $(\text{HSO}_3\text{C}_6\text{H}_4\text{CH}_2)_4\text{Ge}$ was formed¹⁴⁵. In the early 1960s it was shown that the C–Ge bond could be cleaved by AlCl_3 ³²³ and particularly easily by GaCl_3 and InCl_3 .

In 1963 Razuvaev, Vyazankin and coworkers^{324,325} found that alkyl halides in the presence of AlCl_3 cleaved the C–Ge bond in tetraalkylgermanes to give trialkylhalogermanes in good yield. This reaction was later used by other investigators^{326,327}.

In 1931, Schwarz and Lewinsohn¹⁸⁷ first obtained PhGeCl_3 in 75% yield by the cleavage of Ph_4Ge with tetrachlorogermane in an autoclave at 350°C during 36 hours.

The cleavage reactions of the Ge–halogen bond leading to the formation of germanium–pnictogen and germanium–chalcogen bonds are considered in Sections II.F and II.C, respectively. Hence, we only indicate that in 1955 Rochow and Allred³²⁸ found that Me_2GeCl_2 dissociates to $\text{Me}_2\text{Ge}^{2+}$ and 2Cl^- ions in dilute aqueous solutions.

E. Compounds having a Ge–H Bond

The first representative of organogermanium hydrides $\text{R}_{4-n}\text{GeH}_n$ ($n = 1-3$) was triphenylgermane. Kraus and Foster¹⁶¹ obtained it in 1927 by reaction of NH_4Br and triphenylgermylsodium in liquid ammonia. Five years later Kraus and Flood¹⁴⁸ similarly synthesized triethylgermane.

In 1950 the first alkyl germanes RGeH_3 ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, i\text{-Am}$) were obtained by Kraus and coworkers^{214,329} by the reaction of NaGeH_3 and alkyl bromides or chlorides (the same method was also used later^{330,331}). They also synthesized the first dialkylgermane $i\text{-AmEtGeH}_2$ from $i\text{-AmBr}$ and EtGeH_2Li in an ethylamine media (References 330 and 331). Analogously, the reaction of $i\text{-AmEtGeH}_2\text{Li}$ and EtI led to $i\text{-AmEt}_2\text{GeH}$ ^{214,329}.

It is remarkable that according to Kraus^{332,333} the reaction of NaGeH_3 and PhBr in liquid ammonia gave benzene and the monomeric germylene GeH_2 . Onyszchuk³³¹ added H_3GeBr , Me_3GeBr , Me_3SiCl , Me_2SiCl_2 and MeI to NaGeH_3 and obtained the corresponding substituted compounds containing Ge–Ge and Ge–Si bonds.

In 1953, West³³⁴ succeeded in obtaining Ph_3GeH and Me_2GeH_2 by reducing Ph_3GeBr and $(\text{Me}_2\text{GeS})_n$ with zinc amalgam and hydrochloric acid. However, MeGeCl_3 was not reduced by this method.

The most accessible synthesis of organohydrogermanes was based on the reduction of the corresponding organohalogermanes ($R_{4-n}GeX_n$, $n = 1-3$) with complex hydrides such as $LiAlH_4$ ^{173,183,230,237,318,335-342}, $NaBH_4$ ^{276,343}, and $LiAlH(OBu-t)_3$ ^{322,344}. The less reactive lithium hydride and deuteride have been also recommended for this reduction^{270,345}, and sodium hydride in the presence of boron or aluminum derivatives was also used.

The Ge—Cl bonds in $(c-C_6H_{11})_3GeX$ ($X = Cl, Br$) were first reduced with the Ge—H bonds with $LiAlH_4$ in 1947 by Finholt and coworkers³³⁶. Two years later this method of organohydrogermane synthesis was implemented by Johnson and Nebergall²³⁰. In particular, Johnson and Harris¹⁷³ obtained in this way the first diarylgermane Ph_2GeH_2 . Johnson and Nebergall²³⁰ succeeded in reducing the Ge—O bond of $(c-C_6H_{11})_3GeOH$ and $Ph_3GeOGePh_3$ by $LiAlH_4$ to $(c-C_6H_{11})_3GeH$ and Ph_3GeH , respectively.

Lesbre and Satge obtained trialkylgermanes by reducing trialkylalkoxygermanes²⁸⁰, trialkyl(alkylthio)germanes³⁴⁶ and triethyl(diphenylphosphinyl)germane³⁴⁷ with $LiAlH_4$. In 1963, the reduction of the corresponding halides with $LiAlH_4$ gave the optically active organogermanes $RPh(1-C_{10}H_7)GeH$ ($R = Me$ ³⁴⁸, Et ³⁴⁹), which were resolved to the optically active enantiomers.

Triorganylgermanes were also formed by the reaction of $GeCl_4$ and organylmagnesium halides having bulky substituents such as *i*-Pr, 2-MeC₆H₄ and $c-C_6H_{11}$ ^{178,180,319}. The intermediates of this reaction seem to be triorganylgermylmagnesium halides R_3GeMgX , whose hydrolysis gave R_3GeH ¹⁷⁸. Triethylgermane was formed by cleavage of the Ge—M bonds of Et_3GeM ($M = Li, Cd, Hg, Bi$) with water, alcohols or acetic acid^{231,249,350}.

In 1961, Satge and Lesbre^{276,351} used trialkylgermanes in the presence of AlX_3 for partial reduction of R_2GeX_2 ($X = Cl, Br$) to R_2GeHX . An analogous reaction was performed four years earlier in organosilicon chemistry³⁵².

The same authors^{276,351} also synthesized dialkylhalogermanes R_2GeHX ($X = Br, I$) by the reaction of R_2GeH_2 and haloalkanes in the presence of AlX_3 . Again, the analogous organosilicon reaction was reported four years earlier³⁵².

Mironov and Kravchenko³⁵³ suggested an original synthesis of alkylchlorogermanes $RGeHCl_2$ based on alkylation of the $Et_2O \cdot HGeCl_3$ complex with tetraalkylstannanes and tetraalkyl-plumbanes. The reaction with Me_4Sn resulted in 80% yield of $MeGeHCl_2$. The reaction with higher tetraalkylstannanes was complicated with by-processes.

In 1950, Johnson and Harris¹⁷³ found that thermal decomposition of Ph_3GeH gave Ph_2GeH_2 and Ph_4Ge . The diphenyldigermene product was also unstable and decomposed slowly even at room temperature, forming tetraphenylgermane as one of the products. Phenylgermane decomposed to Ph_2GeH_2 and GeH_4 ³⁵⁴ at 200 °C. The reaction proceeded instantly in the presence of $AlCl_3$ even at room temperature. In contrast, the alkylgermanes $R_{4-n}GeH_n$ were more stable and their stability toward thermolysis increased on decreasing the value of n ²⁷⁶. At 400–450 °C tricyclohexylgermane decomposed to elementary germanium, cyclohexene and hydrogen, and at *ca* 360 °C cyclohexane, benzene and polycondensed compounds having $c-C_6H_{11}$ groups were formed³⁵⁵. In contrast, the thermal decomposition of $(c-C_6H_{11})_3SiH$ proceeded at 600–650 °C. Since 1949, it was established that the first products of Ge—H bond oxidation, e.g. of R_3GeH , were triorganylgermanoles R_3GeOH , which then condensed to give digermoxanes $R_3GeOGeR$ ^{230,337,356}.

Kraus, Flood and Foster^{148,161}, and much later other research chemists^{173,183,230,276,357}, discovered that organic germanium hydrides $R_{4-n}GeH_n$ ($n = 1-3$) reacted extremely readily with halogens to form corresponding halides $R_{4-n}GeX_n$ ($X = Cl, Br, I$).

Even in 1927, Kraus and Foster¹⁶¹ showed that triphenylgermane reacted with HCl to give the triphenylchlorogermane. Thirty years later Anderson³³⁷ conducted an analogous

reaction of trialkylgermane, e.g. triethylgermane and hydrochloric acid. HCl and HBr reacted with $RGeH_3$ and R_2GeH_2 only in the presence of $AlCl_3$ or $AlBr_3$ ^{276,358,359}.

In 1953, Anderson³³⁷ found that the reaction of concentrated H_2SO_4 with trialkylgermanes gave hydrogen and bis(trialkylgermyl) sulfates $(R_3GeO)_2SO_2$. According to Satge²⁷⁶, the reaction of Et_3GeH and benzenesulfonic acid leads similarly to Et_3GeOSO_2Ph .

$(Et_3GeO)_3B$ was obtained by the reaction of Et_3GeH and H_3BO_3 in the presence of copper powder³⁶⁰. An analogous reaction of Et_3SiH and H_3BO_3 in the presence of colloidal nickel was reported four years earlier³⁶¹. Bu_3GeH reacts quantitatively with acetic acid³⁶⁰ in the presence of copper. Perfluoroalkancarboxylic acids reacted smoothly with Et_3GeH without any catalyst to form triethylperfluoroacyloxygermanes³³⁷. In contrast, Cl_3CCOOH , Br_3CCOOH and ICH_2COOH were reduced to CH_3COOH by Et_3GeH ³³⁷. Anderson also conducted the reaction of R_2GeH_2 with H_2SO_4 ³³⁷.

In 1962, Lesbre and Satge^{360,362} found that R_3GeH condensed with water or with alcohols, glycols and phenols ($R'OH$) in the presence of copper powder to form hydrogen and R_3GeOH or R_3GeOR' , respectively. The reaction of Bu_2GeH_2 and 1,4-butanediol led to 2,2-dibutyl-1,3-dioxo-2-germacyclopentane³⁶⁰.

Unlike Si—H and especially Sn—H bonds, the Ge—H bond is rather stable to alkaline hydrolysis or alcoholysis³⁶³. For example, $R_{4-n}GeH_n$ (R = alkyl; $n = 1-3$) did not react with a 20% NaOH solution. According to Fuchs and Gilman³¹⁸ trihexylgermane did not react with aqueous-alcoholic KOH solution, whereas Ph_3GeH reacted easily with a similar solution³¹⁸, and $HexGeH_3$ and R_2GeH_2 reacted very slowly at 80 °C²⁷⁶.

Organogermanium hydrides are very good reducing agents. In 1957, Anderson³³⁷ showed that Et_3GeH reduced transition metal salts to their lower valence state (Cu^{II} to Cu^I , Ti^{IV} to Ti^{III} or Ti^{II} , V^{IV} to V^{III} , Cr^{IV} to Cr^{III}) or to the free metals (Au, Hg, Pd, Pt).

In 1961, Satge²⁷⁶ found out that Et_3GeH reduced $GeCl_4$ first to $GeCl_2$ and then to Ge^0 . Nametkin and coworkers used an analogous reaction to reduce $TiCl_4$ to $TiCl_2$ ³⁶⁴. In ether, the reaction gave a $2Et_2O \cdot HGeCl_3$ complex³⁵⁶.

In 1961, it was found that organogermanium hydrides $R_{4-n}GeH_n$ reduced organic halogen derivatives in the absence of catalysts to the corresponding hydrocarbons^{276,351}. The reaction is easier the higher the value of n and the atomic number of the halogen.

Bu_2GeH_2 reduces iodobenzene with greater difficulty than it reduces aliphatic monohalides²⁷⁶. At 220 °C, Bu_3GeH reduces CCl_4 to $HCCl_3$ almost quantitatively²⁷⁶.

Triorganylgermanes readily reduce acyl chlorides^{173,276} and chloromethyl ether, preferably in the presence of traces of $AlCl_3$ ^{276,288,354,356}. In 1964, it was found that organogermanium hydrides also readily reduced N-halosuccinimides^{354,365}.

In 1962, Lesbre and Satge³⁶⁰ pointed out that trialkyl(alkylthio)germanes R_3GeSR' were formed by condensation of trialkylgermanes and thioles in the presence of asbestos platinum. Reduced nickel proved later to be the best catalyst for the reaction³⁴⁶.

In 1966, Vyazankin and Bochkarev³⁶⁶⁻³⁶⁹ found that, depending on the reaction conditions, heating of triethylgermane and elementary sulfur, selenium and tellurium gave the respective triethylgermylchalcogenols Et_3GeEH ($E=S, Se$) or bis(triethylgermyl)chalcogenides $(Et_3Ge)_2E$ ($E = S, Se, Te$). The latter were also formed when diethylselenide^{366,367} and diethyltelluride³⁶⁸ were used instead of Se and Te . The reaction of Et_3GeEH and Et_3SnH afforded unsymmetrical chalcogenides $Et_3GeESnEt_3$ ($E = S, Se$)^{367,368}. Vyazankin and coworkers determined that the M—H bond reactivity with chalcogens increased considerably in the following order for M: Si < Ge < Sn.

F. Organogermanium Chalcogen Derivatives

Organogermanium compounds in which the Ge is bonded to a Group 16 element (chalcogen) were first encountered in 1925, concerning this field of organometallic chemistry.

The first compounds having germoxane Ge—O bonds were Ph_3GeOH , $\text{Ph}_3\text{GeOGePh}_3$ and $(\text{Ph}_2\text{GeO})_4$. In 1925, Morgan and Drew¹⁴⁹ synthesized hexaphenyldigermoxane in quantitative yield by the reaction of aqueous-alcoholic AgNO_3 with Ph_3GeBr . The germoxane quantitatively generated Ph_3GeBr by reaction with concentrated HBr . In 1930, Kraus and Wooster³⁷⁰ obtained $\text{Ph}_3\text{GeOGePh}_3$ by hydrolysis of Ph_3GeNH_2 . They discovered that the digermoxane was cleaved to Ph_3GeONa and Ph_3GeNa by Na in liquid ammonia.

In 1933, Simons and coworkers¹⁶² showed that hexaaryldigermoxanes $\text{Ar}_3\text{GeOGeAr}_3$ ($\text{Ar} = 3\text{-MeC}_6\text{H}_4$, $4\text{-MeC}_6\text{H}_4$) were formed not only by the reaction of aqueous-alcoholic AgNO_3 with Ar_3GeBr , but also by a 0.5N NaOH solution. $(2\text{-MeC}_6\text{H}_4)_3\text{GeCl}$ and aqueous-alcoholic AgNO_3 gave $(2\text{-MeC}_6\text{H}_4)_3\text{GeOH}$. In 1934, Bauer and Burschkies¹⁷² obtained $(\text{PhCH}_2)_3\text{GeOGe}(\text{CH}_2\text{Ph})_3$ by the same method. When concentrated HHal was added to the latter, the corresponding tribenzylhalogermanes were isolated.

In 1930, Dennis and Patnode¹⁶⁷ first reported that self-condensation of trimethylgermanol Me_3GeOH under anhydrous conditions led to $\text{Me}_3\text{GeOGeMe}_3$ which, however, was neither characterized nor examined. In 1961, Schmidt and Ruidisch^{371,372}, Griffiths and Onyszchuk³⁷³ and others in 1966^{374,375} simultaneously synthesized hexamethyldigermoxane by the reaction of Me_3GeX ($\text{X} = \text{Cl}, \text{Br}$) and Ag_2CO_3 . In 1932, Kraus and Flood¹⁴⁸ obtained hexaethyldigermoxane $\text{Et}_3\text{GeOGeEt}_3$ nearly quantitatively by hydrolysis of Et_3GeBr with aqueous KOH or NaOH solutions. It was transformed to the corresponding triethylhalogermanes by reaction with concentrated HCl or HBr . The reaction of $\text{Et}_3\text{GeOGeEt}_3$ and Li gave an equimolar mixture of Et_3GeOLi and Et_3GeLi .

In 1951, Anderson³⁷⁶ obtained hexaethyldigermoxane by reacting Et_3GeBr with Ag_2CO_3 and studied its cleavage by HNCS . Later, he obtained $\text{R}_3\text{GeOGeR}_3$ with $\text{R} = \text{Pr}^{184,315,376}$, $i\text{-Pr}^{184}$, $\text{Bu}^{314,376}$ and investigated their cleavage by organic³⁷⁷ and inorganic^{337,378,379} acids. $\text{Me}_3\text{GeOGeMe}_3$ was even cleaved with such an exotic reagent as $\text{Me}(\text{PO})\text{F}_2^{374}$. Hexaorganyldigermoxanes carrying bulky substituents could not generally be obtained by hydrolysis of the corresponding triorganylhalogermanes. However, they were produced by other methods. For example, in 1953, Anderson¹⁸⁴ synthesized $\text{R}_3\text{GeOGeR}_3$, $\text{R} = i\text{-Pr}$ by the reaction of $i\text{-Pr}_3\text{GeBr}$ and Ag_2CO_3 . The cleavage of hexaisopropyldigermoxanes with inorganic acids HX resulted in $i\text{-Pr}_3\text{GeX}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{NCS}$).

Triphenylgermanol was the first organogermanium compound containing the Ge—OH group. Contrary to expectations, attempts by Morgan and Drew¹⁴⁹ and Kraus and Foster¹⁶¹ to obtain Ph_3GeOH by hydrolysis of Ph_3GeBr had failed and $\text{Ph}_3\text{GeOGePh}_3$ was always the only reaction product. Nevertheless, in 1954, Brook and Gilman¹⁹⁵ obtained high yield of Ph_3GeOH by the reaction of Ph_3GeBr in aqueous-alcoholic KOH . However, Kraus and Foster¹⁶¹ synthesized triphenylgermanol for the first time in 1927 by hydrolysis of Ph_3GeONa or by treating the latter with NH_4Br in liquid ammonia. The Ph_3GeONa was prepared by oxidation of Ph_3GeNa in the same solvent. In 1966, the synthesis of Ph_3GeOH by a slow hydrolysis of $\text{Ph}_3\text{GeH}^{380}$ was reported.

Dennis and Patnode¹⁶⁷ assumed the existence of trimethylgermanol, but neither they nor Schmidt and Ruidisch³⁷¹ succeeded in isolating it. Schmidt and Ruidisch used titrimetric and cryoscopic methods to show that Me_3GeCl was hydrolyzed by water to Me_3GeOH ,

but its attempted isolation from the aqueous solution failed and only $\text{Me}_3\text{GeOGeMe}_3$ was isolated. However, lithium trimethylgermanolate Me_3GeOLi was obtained by cleavage of $\text{Me}_3\text{GeOGeMe}_3$ with methylolithium³⁷². Et_3GeBr hydrolysis had not resulted in triethylgermanol¹⁴⁸ and hexaethyldigermoxane was always formed instead.

It was not possible to isolate trialkylgermanols R_3GeOH with $\text{R} = \text{Me, Et, Pr, Bu}$ until 1970, since they turned out to be considerably less stable than the isostructural trialkylsilanols and trialkylstannanols. Nevertheless, when the germanium atom was bonded to bulky substituents such as *i*-Pr, *c*- C_6H_{11} , 2-Me C_6H_4 and 1- C_{10}H_7 , the corresponding rather stable triorganylgermanols were isolated. Thus, in 1932, Bauer and Burschkies¹⁸¹ synthesized tricyclohexylgermanol by the reaction of $(\text{c}-\text{C}_6\text{H}_{11})_3\text{GeBr}$ with aqueous-alcoholic AgNO_3 . Johnson and Nebergall²³⁰ repeated this reaction after 17 years. Simons and coworkers¹⁶² similarly obtained $(2\text{-MeC}_6\text{H}_4)_3\text{GeOH}$ from the appropriate chloride.

In 1952, West¹⁸³ successfully used for the first time the reaction of R_3GeX for the synthesis of $(1\text{-C}_{10}\text{H}_7)_3\text{GeOH}$. The latter was so stable that it was transformed slowly and partially to the corresponding digermoxane only at 175 °C during 24 hours.

Triisopropylgermanol was first synthesized by Anderson in 1954^{184,381} by hydrolysis of *i*- Pr_3GeBr in aqueous 6N NaOH solution. Later, he used *i*- Pr_3GeCl ³⁷⁹ for obtaining the same product which he obtained by alkali hydrolysis of the reaction products of GeBr_4 with excess *i*- PrMgBr (i.e. *i*- Pr_3GeBr)^{184,337}. The *i*- Pr_3GeOH was then converted to *i*- Pr_3GeX by reaction with HX ($\text{X} = \text{F, Cl, I}$)¹⁸⁴.

Compounds with $\text{R} = \text{Ph}$ were the first representatives of perorganylcyclogermoxanes $(\text{R}_2\text{GeO})_n$ and the corresponding linear polymers $\text{HO}(\text{R}_2\text{GeO})_n\text{H}$. In 1925, Morgan and Drew¹⁴⁹ isolated two products from hydrolysis of Ph_2GeBr_2 which were described as $\text{HO}(\text{Ph}_2\text{GeO})_4\text{H}$ and $(\text{Ph}_2\text{GeO})_4$ and named according to Kipping's nomenclature 'trianhydrotetrakisdiphenylgermanediol' and 'tetraanhydrotetrakisdiphenylgermanediol', respectively.

Five years later Kraus and Brown²²⁶ found out that the solid products of hydrolysis of Ph_2GeBr_2 with concentrated aqueous ammonia have the $(\text{Ph}_2\text{GeO})_n$ structure.

In 1960, Metlesics and Zeiss²¹³ investigated the thermal decomposition of $(\text{Ph}_2\text{GeO})_4$ and $(\text{Ph}_2\text{GeO})_n$ in vacuum, which resulted in $(\text{Ph}_2\text{GeO})_3$. In the same year Brown and Rochow³⁸² similarly obtained $(\text{Me}_2\text{GeO})_3$ from thermolysis of the products of the hydrolysis of Me_2GeCl_2 .

In 1932, Flood¹⁸⁸ isolated two products with a composition of Et_2GeO from the aqueous NaOH hydrolysis of Et_2GeBr_2 . A liquid was identified as hexaethylcyclotrigermoxane $(\text{Et}_2\text{GeO})_3$, where the other, an insoluble solid, was ascribed to the dimer. In 1950, Anderson³⁷⁸ reproduced the experiment, and suggested that the latter was octaethylcyclotetragermoxane $(\text{Et}_2\text{GeO})_4$.

In 1948, Rochow^{252,383} discovered that the hydrolysis product of Me_2GeCl_2 was easily dissolved in water in contrast to the hydrolysis product of Me_2SiCl_2 . The solution was evaporated without leaving any residue, indicating the formation of volatile hydrolysis products. This was also observed in the reaction of Me_2GeCl_2 with aqueous ammonia. This led Rochow to the conclusion that the hydrolysis reaction of Me_2GeCl_2 was reversible.

In 1948, Trautman and Ambrose³⁸⁴ patented a method for producing $(\text{Et}_2\text{GeO})_3$. In 1953, Anderson¹⁸⁴ synthesized $(i\text{-Pr}_2\text{GeO})_3$, the first cyclogermoxane having rather bulky substituents at the Ge atom, by hydrolysis of the reaction products of GeBr_4 and *i*- PrMgBr with aqueous NaOH. Hexaisopropylcyclotrigermoxane cleavage by appropriate acids gave *i*- Pr_2GeX_2 ($\text{X} = \text{F, Cl, Br, I}$).

According to Mazerolles³⁸⁵, the oxidation of germacycloalkanes $(\text{CH}_2)_n\text{GeH}_2$, $n = 4$ gave the corresponding cyclotriggermoxane $[(\text{CH}_2)_4\text{GeO}]_3$ but, when $n = 5$, a mixture of $[(\text{CH}_2)_5\text{GeO}]_4$ and $(\text{CH}_2)_5\text{Ge}(\text{H})\text{OH}$ was formed.

The pioneers of organogermanium chemistry, Morgan and Drew¹⁴⁹, were the first to synthesize polyorganylgermoxanol and polyorganylgermesquioxane, which for a long time were termed organyl germanoic acid and its anhydride, respectively. The amorphous polymer soluble in alkalis, obtained by hydrolysis of PhGeBr_3 , had a composition varying from PhGeO_2H to $\text{PhGeO}_{1.5}$, depending on the reaction conditions. The authors were sure that the product had a structure intermediate between those of phenylgermanoic acid PhGeOOH and its anhydride $(\text{PhGeO})_2\text{O}$.

In 1927, Orndorff, Tabern and Dennis¹⁴⁵ synthesized the aforementioned anhydride, i.e. polyphenylgermesquioxane $(\text{PhGeO}_{1.5})_n$, by treatment of PhGeCl_3 with a dilute aqueous ammonia solution. The anhydride had high solubility in alkalis and could be reprecipitated from the alkali solution by carbon dioxide. Other polyorganylgermesquioxanes $(\text{RGeO}_{1.5})_n$ with $\text{R} = \text{PhCH}_2$, 4-MeC₆H₄ and $\text{Me}_2\text{NC}_6\text{H}_4$ were produced analogously. Five years later Bauer and Burschkies¹⁸¹ described a few more polyorganylgermesquioxanes.

The first polyalkylgermesquioxane $(\text{EtGeO}_{1.5})_n$ was obtained by Flood¹⁸⁸ as a by-product of a reaction that he investigated. A year later he synthesized it by the reaction of EtGeI_3 and Ag_2O or by hydrolysis of $(\text{EtGeN})_n$, the product of ammonolysis of EtGeI_3 ³⁰⁶. In 1939, Tchakirian³⁸⁶ obtained 'alkylgermanium acids' RGeOOH ($\text{R} = \text{Me}$, Et) by hydrolysis of RGeCl_3 . Analogously, 'germanomalonic acid' $\text{CH}_2(\text{GeOOH})_2$ was synthesized from $\text{CH}_2(\text{GeCl}_3)_2$.

Organoxy and acyloxy derivatives having $\text{Ge}-\text{OR}$ and $\text{Ge}-\text{OOCR}$ groups as well as a heterogermoxane $\text{Ge}-\text{OM}$ group ($\text{M} = \text{a metal or a nonmetal atom}$) belong to organogermanium compounds with germoxane bonds. In 1949, Anderson³⁸⁷ reported the formation of alkylalkoxygermanes $\text{Et}_{4-n}\text{Ge}(\text{OR})_n$ ($\text{R} = \text{Me}$, Et , Bu ; $n = 1, 2$) during the reaction of $\text{Et}_{4-n}\text{Ge}(\text{NCO})_n$ and the appropriate alcohols; he did not isolate or characterize the compounds. In 1954, West and coworkers³⁸⁸ described the synthesis of all the methylmethoxygermanes by the reaction of Me_3GeI , Me_2GeCl_2 and MeGeCl_3 with sodium methoxide. In 1956, Anderson³⁸⁹ also synthesized the first trialkylaryloxygermanes $\text{Et}_3\text{GeOC}_6\text{H}_4\text{R}$ ($\text{R} = 3\text{-Me}$, 2-NH_2)³⁸⁹. As early as in 1962, Lesbre and Satge³⁶⁰ produced the Et_3GeOPh , the simplest representative of this series. $\text{Et}_3\text{GeOCH}_2\text{Ph}$ ²⁸⁰ was synthesized at the same time²⁸⁰. In 1961, Griffiths and Onyszchuk³⁷³ similarly obtained Me_3GeOMe . In 1954, Brook and Gilman¹⁹⁵ pointed out that one of the first arylalkoxygermanes Ph_3GeOMe was the thermal decomposition product of $\text{Ph}_3\text{GeCOOMe}$ at 250°C with CO elimination. For comparison, triphenylmethoxygermane was synthesized from Ph_3GeBr and MeONa . In 1968, Peddle and Ward³⁹⁰ discovered the rearrangement of $\text{Ph}_3\text{GeCH}_2\text{OH}$ to Ph_3GeOMe .

In 1961, Griffiths and Onyszchuk³⁷³ found that the reaction of MeGeH_2Br and MeONa at -80°C gave MeGeH_2OMe , which slowly decomposed to form the polymer $(\text{MeGeH})_n$ and MeOH .

In 1962, two new approaches to trialkylalkoxygermane were introduced at the Satge laboratory³⁶. The first was based on the dehydrocondensation of trialkylgermanes and alcohols or glycols. Using R_2GeH_2 led not only to $\text{R}_2\text{GeOR}'_2$, but also to $\text{R}_2\text{GeHOR}'$. Dehydrocondensation of Bu_2GeH_2 with $\text{HO}(\text{CH}_2)_4\text{OH}$ resulted in 2,2-dibutyl-1,3-dioxo-2-germacycloheptane. A year later Wieber and Schmidt³⁹¹ synthesized one of the simplest heterocyclic systems, 2,2-dimethyl-1,3-dioxo-2-germacyclopentane, by the reaction of Me_2GeCl_2 and ethylene glycol in the presence of Et_3N . They also produced the benzyl

derivatives of 2,2-dimethyl-1,3-dioxo-2-germacyclopentane and 2,2-dimethyl-1,4-dioxo-2-germacyclohexane³⁹². The second approach²⁸⁰ to compounds R_3GeOR' was the addition reaction of R_2GeH to carbonyl compounds in the presence of copper powder.

In 1964, Satge³⁶² used a re-alkoxylation reaction, with alcohols having boiling points higher than those of MeOH or EtOH, to replace the alkoxy group in R_3GeOR' ($R' = Me, Et$) by another alkoxy group. This method was used later by other investigators^{390,393–395}.

Mehrotra and Mathur³⁹⁶ in 1966 investigated extensively the cleavage reaction of $Bu_3GeOGeBu_3$, $(Bu_2GeO)_n$ and $(Ph_2GeO)_n$ by alcohols, glycols, mono-, di-, and triethanolamine and acetylacetone (which apparently reacted via its enol form). Diverse noncyclic and cyclic compounds having $Ge-O-C$ groups were produced. Voronkov and coworkers^{397,398} first obtained 1-organylgermantranes $RGe(OCH_2CH_2)_3N$ ($R = Alk, Ar$) by cleavage of $(RGeO_{1.5})_n$ with triethanolamine.

In 1962, Lesbre and Satge²⁸⁰ demonstrated that the $Ge-O$ bond in alkylalkoxygermanes was cleaved with HI, RCOOH, Ac_2O , $PhCOCl$, $PhSO_2OH$ and $LiAlH_4$ much more easily than that of the $Ge-O-Ge$ group.

Organogermanium peroxides $Pr_3GeOOCMe_3$, $Pr_3GeOOC_{10}H_{17}-1$, $Pr_2Ge(OOC_{10}H_{17})_2$ and $Pr_3GeOOGePr_3$ ($1-C_{10}H_{17} = 1$ -decalyl) having the germperoxane $Ge-O-O$ group were first synthesized by Davies and Hall^{399,400}. They were produced by the reaction of the appropriate hydroperoxide with Pr_3GeCl or with Pr_2GeCl_2 in the presence of a tertiary amine. A year later Rieche and Dahlmann⁴⁰¹ synthesized Ph_3GeOOR and $Ph_3GeOOGePh_3$ from Ph_3GeBr , NH_3 and $ROOH$ with $R = CPh_{3-n}Me_n$ ($n = 1-3$).

Johnson and Nebergall²³⁰ discovered the series of organylacyloxygermanes; they synthesized $(c-C_6H_{11})_3GeOOCCH_3$ by the reaction of tricyclohexylgermanol and acetic anhydride.

In 1950, Anderson³⁷⁸ obtained alkylacyloxygermanes $Et_{4-n}Ge(OOCR)_n$ ($R = H, Me, CH_2SGeEt_3$; $n = 1, 2$) by cleavage of $Et_3GeOGeEt_3$ or $(Et_2GeO)_n$ by carboxylic acids or by their anhydrides. Within a year he used $Pr_3GeOGePr_3$ ⁴⁰² in these reactions. However, his attempt to cleave germoxanes $R_3GeOGeR_3$ and $(R_2GeO)_3$ with $R = i-Pr$ by carboxylic acids was unsuccessful¹⁸⁴. However, he later succeeded in obtaining the expected products $i-Pr_2Ge(OOCR)_2$ with $R = Me, Et, Pr, Bu$ by the reaction of $i-Pr_2GeX_2$ and the silver salts of the corresponding carboxylic acids³⁷⁹. He used a similar reaction of Et_3GeBr and $ArCOOAg$ for the synthesis of $Et_3GeOOCAr$ ($Ar = Ph, 2-H_2NC_6H_4$)³⁸⁹. Tributylacyloxygermanes could also be prepared by the reaction of Bu_3GeI and $RCOOAg$ ³¹⁴.

However, silver chloroacetate and benzoate did not react with Et_3GeCl . Anderson³⁸¹ recommended the reaction of $i-Pr_3GeCl$ with $RCOOAg$ as the best method for synthesis of $i-Pr_2GeOOCR$. During the synthesis of trialkylacyloxygermanes he discovered that a thermal decomposition of $i-Pr_3GeOOCCH_2CH_2Cl$ gave $i-Pr_3GeCl$ and $CH_2=CHCOOH$ ³⁸¹. For $Et_3GeOOCH$ synthesis he used lead formate³¹⁷.

In 1956, Anderson³⁷⁹ studied the reaction of $MeCOOAg$ with a series of Et_3GeX ($X = I, Br, Cl, H, SR_3, CN, NCS, NCO, OGeR_3$). He found that the reactivity of the $Ge-X$ bond in R_3GeX ($R = Et, i-Pr$) with respect to silver salts decreased in the following order of X : $I > SGeR_3 > Br > CN > Cl > NCS > NCO > OGeR_3 \geq OCOR \gg F$ ('the Anderson row').

In 1951, Anderson⁴⁰² first carried out the re-esterification reaction of organylacyloxygermanes with carboxylic acids. He also studied esterification of R_3GeOH with carboxylic acids ($R'OOH$) leading to $R_3GeOOCR'$ in the presence of anhydrous Na_2SO_4 or with H_2SO_4 ³⁸¹.

In 1957, Anderson found that perfluoroalkanoic acids dehydrocondense with Et_3GeH without catalyst to give $Et_3GeOOCR$ ($R = CF_3, C_2F_5, C_3F_7$), whereas the reaction did

not occur with acetic acid. In the reaction with Et_3GeH the RCOOH ($\text{R} = \text{Cl}_3\text{C}$, Br_3C , ICH_2) behaved in a quite different manner and were reduced to CH_3COOH ³³⁷.

In the period of 1951 till 1957, Anderson enriched the acyloxygermane chemistry by sixty-six compounds $\text{R}_{4-n}\text{Ge}(\text{OOCR}')_n$ with $\text{R} = \text{Et}$, Pr , $i\text{-Pr}$, Bu , $c\text{-C}_6\text{H}_{11}$; $\text{R}' = \text{H}$, Alk , Ar , haloalkyl; $n = 1\text{--}3$ ^{184,314,317,377–379,381,402,403}.

In 1962, Lesbre and Satge³⁶⁰ discovered that the dehydrocondensation reaction of trialkylgermane and carboxylic acids could be catalyzed by copper powder. For instance, the reaction of Bu_3GeH and MeCOOH gave $\text{Bu}_3\text{GeOOCMe}$ in 60% yield.

In 1954, Brook and Gilman synthesized $\text{Ph}_3\text{GeOOCGePh}_3$ by the reaction of Ph_3GeBr and $\text{Ph}_3\text{GeCOONa}$ ¹⁹⁵.

A year later Brook⁴⁰⁴ discovered that under short heating to 200 °C triphenylgermanecarboxylic acid Ph_3GeCOOH eliminated CO and H_2O and transformed to $\text{Ph}_3\text{GeOOCGePh}_3$. Further heating of the latter afforded $\text{Ph}_3\text{GeOGePh}_3$ ⁴⁰⁵. Evidently, Ph_3GeOH was an intermediate product in the initial stage of the thermolysis.

The first organogermanium compounds having a metal-germoxane Ge-O-M group were alkali metal triorganylgermanolates R_3GeOM ($\text{R} = \text{Ph}$, Et ; $\text{M} = \text{Li}$, Na , K) produced in 1925–1932 by Morgan and Drew¹⁴⁹, as well as by Kraus and coworkers^{148,161}. Later, they and many other investigators obtained and used Li and Na germanolates and R_3GeOMgX for synthetic purposes.

Among heterogermoxanes in which the germanium atom was bonded via oxygen to a nonmetal (metalloid) atom, bis(trialkylgermyl)sulfates $(\text{R}_3\text{GeO})_2\text{SO}_2$ with $\text{R} = \text{Et}$, Pr , $i\text{-Pr}$ ^{337,378,381,402} and cyclic dialkylgermylene sulfates $(\text{R}_2\text{GeOSO}_2\text{O})_2$ with $\text{R} = \text{Me}$, Et , Pr , $i\text{-Pr}$ ^{317,379,406} were the first to be synthesized by Anderson in 1950–1956. For the synthesis of compounds with $\text{R} = \text{Et}$, the reactions of H_2SO_4 with $\text{Et}_3\text{GeOGeEt}_3$ and $(\text{Et}_2\text{GeO})_4$ ³⁷⁸ were first used. Later, $(\text{R}_3\text{GeO})_2\text{SO}_2$ and $(\text{R}_2\text{GeOSO}_2\text{O})_2$ with $\text{R} = \text{Me}$, Et , Pr , $i\text{-Pr}$ were obtained by the reaction of H_2SO_4 with $\text{R}_3\text{GeOOCMe}$, $i\text{-Pr}_3\text{GeOH}$ and $\text{R}_2\text{Ge}(\text{OOCMe})_2$ ^{379,389,402,406}. Anderson³³⁷ used the reactions of Et_3GeH and H_2SO_4 or HgSO_4 for synthesis of bis(triethylgermyl) compounds. In 1951, he also produced the first organogermanium compound having a Ge-O-N group, i.e. $\text{Et}_3\text{GeONO}_2$ by the reaction of Et_3GeBr and AgNO_3 ³⁷⁶. In 1955, Rochow and Allred³²⁸ obtained $\text{Me}_2\text{GeCrO}_4$, isostructural to $(\text{R}_2\text{GeSO}_4)_2$ by the reaction of Me_2GeCl_2 and K_2CrO_4 in aqueous media.

In 1961, Satge²⁷⁶ carried out the dehydrocondensation of Et_3GeH and PhSO_3H , which resulted in $\text{Et}_3\text{GeOSO}_2\text{Ph}$.

In 1950–1967 Schmidt, Schmidbaur and Ruidisch synthesized a large series of heterogermoxanes having Ge-O-M groups with $\text{M} = \text{B}$, Al ⁴⁰⁷, Ga ⁴⁰⁸, In ⁴⁰⁸, Si ^{405,409}, N ^{410,411}, P ^{410,412}, As ⁴¹³, S ⁴⁰⁵, Se ^{412,413}, Cl ⁴¹⁴, V ⁴¹², Cr ⁴⁰⁹ and Re ⁴¹². Those were mostly the trimethylgermyl esters of the corresponding inorganic acids such as $(\text{Me}_3\text{GeO})_n\text{Y}$ with $\text{Y} = \text{NO}_2$, ClO_3 , ReO_3 ($n = 1$); SO_2 , SeO_2 , CrO_2 ($n = 2$); B , PO , AsO , VO ($n = 3$). They were produced by hexamethyldigermoxane cleavage with anhydrides of inorganic acids: P_2O_5 ⁴¹⁰, As_2O_5 ⁴¹³, SO_3 ⁴⁰⁵, SeO_3 ^{412,413}, V_2O_5 ⁴¹², CrO_3 ^{409,412} and Re_2O_7 ⁴¹². The same types of compounds were synthesized by reaction of Me_3GeCl with the silver salts of the corresponding acids^{410,412,413}. Similarly, Srivastava and Tandon prepared $(\text{Ph}_3\text{GeO})_2\text{Y}$ with $\text{Y} = \text{SO}_2$ and SeO_2 ⁴¹⁵.

In 1961–1964 Schmidbaur, Schmidt and coworkers^{405,416}, synthesized a series of compounds $\text{R}_{4-n}\text{Ge}(\text{OSiR}')_n$ with R , $\text{R}' = \text{Me}$, Et ; $n = 1\text{--}3$. For example, trimethyl(trimethylsiloxy)germane $\text{Me}_3\text{GeOSiMe}_3$ and dimethylbis(trimethylsiloxy)germane $\text{Me}_2\text{Ge}(\text{OSiMe}_3)_2$ were obtained by the reaction of alkali metal trimethylsilanolates Me_3SiOM and Me_3GeCl or Me_2GeCl_2 . Schmidbaur and Schmidt⁴⁰⁹ studied the cleavage of trimethyl(trimethylsiloxy)germane with sulfuric and chromic anhydrides (SO_3 and CrO_3), which gave $\text{Me}_3\text{GeOSO}_2\text{OSiMe}_3$ and $\text{Me}_3\text{GeOCrO}_2\text{OSiMe}_3$, respectively. When

$\text{Me}_3\text{GeOSiMe}_3$ reacts with AlCl_3 ⁴⁰⁷ and POCl_3 ⁴¹², only the Si—O bond cleaves, thus leading to $\text{Me}_3\text{GeOAlCl}_2$ and $\text{Me}_3\text{GeOPOCl}_2$, respectively.

By dehydrocondensation of $\text{B}(\text{OH})_3$ with Et_3GeH in 1962 Lesbre and Satge³⁶⁰ obtained tris(triethylgermyl)borate $(\text{Et}_3\text{GeO})_3\text{B}$.

Cleavages of the Ge—O bond in Ge—O—Ge and Ge—O—Si groups are much easier than that for Si—O—Si groups^{417,418}. This indicates that the Ge—O bond is highly reactive. However, the heterolytic cleavage of Sn—O and Pb—O bonds was much easier (see Sections III and IV) than that for the Ge—O bond.

In 1967 Armer and Schmidbaur⁴⁰⁸ obtained metallogermoxanes $(\text{Me}_3\text{GeOMMe}_3)_2$ with $\text{M} = \text{Al}, \text{Ga}, \text{In}$ as well as $(\text{Me}_3\text{GeOGaPh}_2)_2$, $(\text{Ph}_3\text{GeOGaMe}_2)_2$ and $(\text{Ph}_3\text{GeOGaPh}_3)_2$. All these compounds seemed to be dimers. Subsequently, Davies and coworkers⁴¹⁹ synthesized the similar tin and lead derivatives $\text{Ph}_3\text{GeOSnEt}_3$ and $\text{Ph}_3\text{GeOPbPh}_3$.

Organogermenes possessing a germthiane Ge—S bond were first prepared at the Dennis laboratory in 1927¹⁴⁵. These were three-dimensional polyarylgermosesquithianes $(\text{RGeS}_{1.5})_n$ with $\text{R} = \text{Ph}, 4\text{-MeC}_6\text{H}_4, \text{Et}_2\text{NC}_6\text{H}_4$, produced by the action of H_2S on the corresponding $(\text{RGeO}_{1.5})_n$. At the time the compounds were considered to be the sulfur analogs of anhydrides of arylgermanic acids, $(\text{RGe}=\text{S})_2\text{S}$.

Five years later a series of organylgermsesquithianes $(\text{RGeS}_{1.5})_n$ ($\text{R} = \text{Ph}, 4\text{-MeC}_6\text{H}_4, 1\text{-C}_{10}\text{H}_7, \text{Me}_2\text{NC}_6\text{H}_4, \text{Et}_2\text{NC}_6\text{H}_4$) was synthesized by the same method by Bauer and Burschkies¹⁸¹ and later by an easier method by Reichle⁴²⁰.

In 1967, when studying the reaction of MeGeBr_3 and H_2S in the presence of Et_3N , Moedritzer⁴²¹ prepared oligomeric $(\text{MeGeS}_{1.5})_4$, apparently of tetrahedral structure.

Cyclic perorganylcyclogermthiane oligomers $(\text{R}_2\text{GeS})_n$ became known much later. In 1948–1950 Rochow^{251,252} obtained the first $(\text{Me}_2\text{GeS})_n$ by the reaction of H_2S and Me_2GeCl_2 in a 6N H_2SO_4 solution. The crystalline product which has a specific pepper and onion smell was slowly hydrolyzed to H_2S when exposed to atmospheric moisture, and also in boiling water. In dilute acids the hydrolysis is much faster. This was patented later^{422,423}, Brown and Rochow⁴²⁴ found subsequently that the compound was a trimer, i.e. hexamethylcyclotrigermthiane, $(\text{Me}_2\text{GeS})_3$, having the same structure in solution and in the gas phase. In 1963, Ruidisch and Schmidt⁴²⁵ also produced $(\text{Me}_2\text{GeS})_3$ by reaction of H_2S with Me_2GeCl_2 in the presence of Et_3N .

In 1956, Anderson³⁷⁹ synthesized the first four-membered tetraisopropylcyclodigermidithiane $(i\text{-Pr}_2\text{GeS})_2$ by the reaction of $i\text{-Pr}_2\text{GeI}_2$ with Ag_2S . In 1965 its analog $(\text{Bu}_2\text{GeS})_2$ was obtained by passing gaseous H_2S through a solution of $\text{Bu}_2\text{Ge}(\text{OR})_2$ ($\text{R} = \text{Bu}, i\text{-Bu}$) in the corresponding alcohol⁴²⁶. When $\text{R} = t\text{-Bu}$ the reaction occurred only in the presence of PhSO_3H .

In 1963, Schmidt and Schumann⁴²⁷ found that heating Bu_4Ge with sulfur at 250°C gave $(\text{Bu}_2\text{GeS})_3$ and Bu_2S . $\text{Bu}_{4-n}\text{GeSBU}_n$, $n = 1, 2$ were the intermediate products. A similar reaction of sulfur and Ph_4Ge at 270°C gave elementary germanium and Ph_2S , the final thermolysis products of the intermediate $(\text{Ph}_2\text{GeS})_3$ ⁴²⁷. The latter was first obtained by Reichle⁴²⁰ in 1961 by the reaction of $(\text{Ph}_2\text{GeO})_3$ with H_2S *in statu nascendi* in aqueous media. In 1963, Henry and Davidson⁴²⁸ obtained $(\text{Ph}_2\text{GeS})_n$ with $n = 2, 3$ by the reaction of $\text{Ph}_2\text{Ge}(\text{SNa})_2$ and PhCOCl .

Investigations of the chemical transformations of $(\text{R}_2\text{GeS})_n$ started in 1953. West³³⁴ succeeded in reducing $(\text{Me}_2\text{GeS})_3$ to Me_2GeH_2 by reaction with zinc amalgam and HCl in an alcoholic media. In 1956, Anderson³⁷⁹ described the reactions of $(i\text{-Pr}_2\text{GeS})_2$ with silver bromide, cyanide and acetate. Moedritzer and van Wazer⁴²⁹ investigated the exchange reactions of $(\text{Me}_2\text{GeS})_3$ with Me_2GeX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), and with $(\text{Me}_2\text{SiS})_3$ ⁴³⁰.

Monomeric organogermanium compounds having digermthiane (Ge—S—Ge) groups, i.e. hexaorganyl digermthianes $\text{R}_3\text{GeSGeR}_3$, $\text{R} = \text{Et}, \text{Ph}, 4\text{-MeC}_6\text{H}_4, 4\text{-PhC}_6\text{H}_4$ and

PhCH_2 , were produced for the first time by Burschkies⁴³¹ in 1936 via the reaction of the corresponding R_3GeBr with aqueous or alcoholic Na_2S solutions. The reaction of $(c\text{-C}_6\text{H}_{11})_3\text{GeBr}$ and Na_2S resulted in hexacyclohexyldigermperthiane $(c\text{-C}_6\text{H}_{11})_3\text{GeSSGe}(\text{C}_6\text{H}_{11-c})_3$.

In 1956, Anderson³⁷⁹ synthesized $(i\text{-Pr})_3\text{GeSGe}(i\text{-Pri})_3$ by reacting Ag_2S with $i\text{-Pr}_3\text{GeI}$. In 1965–1966, Satge and Lesbre³⁴⁶ and Cumper and coworkers⁴³² produced hexaalkyldigermthianes $\text{R}_3\text{GeSGeR}_3$, $\text{R} = \text{Et}, \text{Bu}$ in high yield by the same method.

In 1966 Abel, Brady and Armitage⁴³³, and in 1968 Wieber and Swarzmman⁴³⁴ used the reaction of triorganylhalogermanes with H_2S in the presence of nitrogen bases for the synthesis of hexaorganyldigermthianes in analogy to the widely used method in organosilicon chemistry.

In 1963, Ruidisch and Schmidt⁴²⁵ discovered that the thermal decomposition of lithium trimethylgermanthiolate afforded $\text{Me}_3\text{GeSGeMe}_3$ and Li_2S . They found that $\text{Me}_3\text{GeSSiMe}_3$ thermally disproportionated to $\text{Me}_3\text{GeSGeMe}_3$ and $\text{Me}_3\text{SiSSiMe}_3$. In 1966, Vayzankin and coworkers^{367,368} decomposed Et_3GeSH at 130°C to H_2S and $\text{Et}_3\text{GeSGeEt}_3$. The latter product also produced in the reaction of Et_3GeSH with Et_2Hg ³⁶⁹. Finally, hexaorganyldigermthianes $\text{R}_3\text{GeSGeR}_3$ were obtained by the reaction of R_3GeSLi with R_3GeX ($\text{R} = \text{Me}, \text{Ph}$; $\text{X} = \text{Cl}, \text{Br}$)^{247,425}.

In 1962, Henry and Davidson⁴³⁵ synthesized octaphenyltrigermdithian $\text{Ph}_3\text{GeSGePh}_2\text{SGePh}_3$, one of the first perorganylligogermdithianes. They also obtained hexaphenyl-digermperthiane $\text{Ph}_3\text{GeSSGePh}_3$ having a Ge-S-S-Ge group by the oxidation of Ph_3GeSH ^{428,435} with iodine. We note that the first compound of this type $c\text{-Hex}_3\text{GeSSGeHex-c}_3$ was described by Burschkies⁴³¹ as early as 1936.

The trialkylgermylthio derivatives of Group 14 elements R_3GeSMR_3 ($\text{M} = \text{Si}, \text{Sn}, \text{Pb}$) are analogs of hexaalkyldigermthiane. They were first synthesized in the Schmidt laboratory^{247,425,436}. For example, R_3GeSMR_3 ($\text{M} = \text{Si}, \text{Sn}, \text{Pb}$; $\text{R} = \text{Me}, \text{Ph}$) was obtained by the reaction of R_3GeSLi with R_3MCl . Unsymmetrical compounds $\text{R}_3\text{GeSMR}'_3$ were obtained by the reaction of R_3GeSLi with $\text{R}'_3\text{MX}$ ($\text{M} = \text{Si}, \text{Sn}$)⁴³⁶. In 1966, Vayzankin and coworkers³⁶⁸ obtained $\text{Et}_3\text{GeSSnEt}_3$ by dehydrocondensation of Et_3GeSH and Et_3SnH .

Triorganyl(organylthio)germanes $\text{R}_3\text{GeSR}'$ should be considered as organogermanium compounds having a Ge-S-M group, when $\text{M} = \text{C}$. Anderson³⁸⁹ was the first to synthesize nine representatives of the Et_3GeSR series by heterofunctional condensation of triethylacetoxgermanes with aliphatic and aromatic thiols RSH , $\text{R} = \text{Alk}, \text{Ar}(\text{C}_6\text{--C}_{12})$.

In 1956, Anderson³⁸⁹ obtained triethyl(organylthio)germanes by cleavage of $\text{Et}_3\text{GeOGeEt}_3$ with aromatic and aliphatic thiols. Later, Satge and Lesbre³⁴⁶ used this reaction for synthesis of Et_3GeSBu . In 1966, Abel and coworkers⁴³³ employed the reaction for the preparation of $\text{Me}_3\text{GeSCMe}_3$ from $\text{Me}_3\text{GeOGeMe}_3$ and Me_3CSH . They also demonstrated that the reaction of Me_3GeOEt and PhSH resulted in Me_3GeSPh . Satge and Lesbre³⁴⁶ obtained Bu_3GeSPh , $\text{Bu}_3\text{GeSC}_8\text{H}_{17-n}$ and $\text{Et}_2\text{Ge}(\text{SPh})_2$ by the reaction of PhSH or $n\text{-C}_8\text{H}_{17}\text{SH}$ with Bu_3GeOMe and $\text{Et}_2\text{Ge}(\text{OMe})_2$. They also cleaved $(\text{Et}_3\text{GeO})_n$ with thiophenol to form $\text{Et}_2\text{Ge}(\text{SPh})_2$. Similar transformations of a Si-O bond to a Si-S bond did not occur with organosilicon compounds. Anderson^{377,389} discovered re-thylation of trialkyl(organylthio)germanes by higher alkanethiols and arenethiols. This process occurred smoothly only on heating $>170^\circ\text{C}$ and when a sufficiently wide range exists between the boiling points of the starting and the resultant thiols³⁴⁶. Following Anderson^{377,389}, other researchers^{346,347,375} used this reaction. Ph_3GeSH ⁴²⁸ was also used in the reaction. The re-thylation reaction resembles the reaction of PhSH with $\text{Et}_3\text{GeSGeEt}_3$ at $180\text{--}190^\circ\text{C}$ which gives Et_3GeSPh and H_2S ³⁴⁶.

Satge and Lesbre³⁴⁶ used the reaction of thiols with R_3GeNMe_2 for the synthesis of triorganyl(alkylthio)germanes R_3GeSR' ($R = i\text{-Pr}, t\text{-Bu}, \text{Octyl}$; $R' = \text{Bu}$). A year after, Abel, Armitage and Brady³⁷⁵ employed the reaction of Me_3GeNEt_2 and $BuSH$ to produce Me_3GeSBu .

In 1962, Davidson, Hills and Henry⁴³⁷ obtained triphenyl(organylthio)germanes Ph_3GeSR by the reaction of Ph_3GeSNa with organic halides ($R = \text{Me}, \text{Bu}, \text{CH}_2\text{Ph}, \text{COPh}, \text{CH}_2\text{SMe}$), and by reaction of the latter halides with Ph_3GeSH in the presence of pyridine. For the synthesis of organyl(organylthio)germanes $R_{4-n}Ge(SR')_n$ ($n = 1, 2$) the reactions of organogermanium halides with mercaptanes or with sodium mercaptides $RSNa$ ^{369,375} in the presence of organic bases^{369,438} were used. The reaction of Me_3GeSLi and Me_3CSH resulting in $Me_3GeSCMe_3$ was also described. Lead alkanethiolates $Pb(SR')_2$ with $R' = \text{Et}, \text{Bu}$ ^{346,369,429} were also employed for the synthesis of $R_{4-n}Ge(SR')_n$ ($n = 1, 2$) from $R_{4-n}GeX_n$ ($X = \text{Cl}, \text{Br}$). Abel, Armitage and Brady³⁷⁵ succeeded in substituting the bromine atom in Me_3GeBr by an alkylthio group by the action of Me_3SiSR ($R = \text{Et}, i\text{-Pr}$).

By using dimethyldichlorogermane and aliphatic or aromatic dithiols, Wieber and Schmidt^{391,392,439} designed new heterocyclic systems in 1963–1964. In 1968, the reaction of Me_2GeCl_2 with $HS(CH_2)_nSH$ ($n = 2, 3$) in the presence of Et_3N enabled them to obtain the first of 2,2-dialkyl-1,3-dithia-2-germacycloalkanes^{392,439}. By the reaction of Me_2GeCl_2 or $MeCH_2(Cl)GeCl_2$ with 4-methylbenzene-1,2-dithiol in the presence of Et_3N they produced the two isomeric ring-methyl derivatives 2,2-dimethyl-4,5-benza-1,3-dithia-2-germacyclopentane and 2-chloro-2-dimethyl-5,6-benza-1,4-dithia-2-germacyclohexane, respectively³⁹². Similarly, 2,2-dimethyl-1-oxa-3-thia-2-germacyclopentane³⁹¹ was obtained from 2-mercaptoethanol.

In 1962, Lesbre and Satge³⁶⁰ first carried out the dehydrocondensation of organogermanium compounds having the $Ge-H$ bond with thiols, by reacting Ph_3GeH with $BuSH$ in the presence of a platinum catalyst to give Ph_3GeSBu . They later used this reaction in the presence of nickel catalyst³⁴⁶. Thus, $Et_3GeSCH_2CH_2SGeEt_3$ was formed by the dehydrocondensation reaction of Et_3GeH with $HSCH_2CH_2SH$. In addition, Satge and Lesbre³⁴⁶ discovered that triethylgermane cleaved $MeSSMe$ to give Et_3GeSMe and $MeSH$.

Several reactions of triorganyl(alkylthio)germanes were investigated in 1962–1965. The $Ge-S$ bond in these compounds was found to be chemically more stable than an $Si-S$ bond, but much more reactive than $Sn-S$ and $Pb-S$ bonds. According to Satge and Lesbre³⁴⁶ and Hooton and Allred⁴⁴⁰, long exposure of triorganyl(alkylthio)germanes (Et_3GeSBu ³⁴⁶, Me_3GeSMe and Ph_3GeSMe ⁴⁴⁰) to water either caused no change or only a slight hydrolysis (for Et_3GeSMe)³⁴⁶. The alcoholysis of R_3MSR' ($M = \text{Ge}$) was much more difficult than that for $M = \text{Si}$ ^{346,440}. Compounds R_3GeSR' are easily oxidized by hydrogen peroxide up to $R_3GeOGeR_3$ ⁴⁴⁰; $LiAlH_4$ reduces them to R_3GeH ³⁴⁶ and aniline does not react with them. The $Ge-S$ bond of Ph_3GeSMe was so reactive that it was cleaved with methyl iodide to Ph_3GeI and $Me_3S^+I^-$ ⁴⁴⁰. Similarly, dimethyl sulfate transforms Me_3GeSMe to Me_3GeOSO_2OMe ⁴⁴⁰ and $Me_3S^+[MeSO_4]^-$. When organolithium or organomagnesium compounds $R'M$ ($R' = \text{alkyl}$; $M = \text{Li}$ ⁴³⁵, MgX ³⁴⁶) reacted with R_3GeSMe ($R = \text{Et}, \text{Ph}$), the SMe group was replaced by alkyl groups giving R_3GeR' derivatives.

Triorganylgermanethiols R_3GeSH were latecomers in organogermanium chemistry. The first representative of this class, i.e. Ph_3GeSH , was produced only in 1963 by Henry and Davidson⁴²⁸ by the reaction of Ph_3GeBr with H_2S in the presence of pyridine.

In 1966, Vyazankin and coworkers^{367,368} found that triethylgermanethiol Et_3GeSH was formed by heating Et_3GeH with sulfur at 140°C . Attempts of Henry and Davidson⁴²⁸ to obtain diphenylgermanedithiol from Ph_2GeBr_2 had failed, although they suggested that a rather labile $Ph_2Ge(SH)_2$ could exist in the reaction mixture.

The first alkali metal triorganylgermanethiolate R_3GeSM was Ph_3GeSNa , synthesized by Henry, Davidson and coworkers^{435,437} by the reaction of Ph_3GeBr with excess Na_2S in an alcoholic solution.

Ruidisch and Schmidt^{425,441} developed a new synthesis of lithium trimethylgermanethiolate Me_3GeSLi in quantitative yield by the reaction of $(Me_2GeS)_3$ with $MeLi$. Later, Vyazankin and coworkers³⁶⁹ produced the analog Et_3GeSLi by the reaction of Li with Et_3GeSH in THF. Ph_3GeSLi was synthesized by the reaction of Ph_3GeLi with sulfur in THF^{247,436,442,443}. Unlike the labile $Ph_2Ge(SH)_2$, its di-sodium salt, which was isolated by Henry and Davidson⁴²⁸ as the trihydrate $R_2Ge(SNa)_2 \cdot 3H_2O$ from the reaction of Ph_2GeBr_2 with Na_2S , turned out to be rather stable.

The chemical transformations of Et_3GeSH and Ph_3GeSH have been extensively investigated by Vyazankin and coworkers^{367,368} and by Henry and Davidson⁴²⁸. The latter authors showed that the reaction of Ph_3GeSH with $PhCOCl$ and $(SCN)_2$ resulted in $Ph_3GeSCOPh$ and Ph_3GeSCN , respectively. They failed in an attempted addition of Ph_3GeSH to an activated double bond.

Organogermanium compounds with Ge—Se bond were prepared much later than their sulfur analogs. All of them were obtained in Schmidt's and the Vyazankin's laboratories. The first compound was hexamethylcyclotrigermeselenane $(Me_2GeSe)_3$, which Schmidt and Ruf⁴⁴⁴ obtained by the reaction of Me_2GeCl_2 with Na_2Se in 1961, together with higher cyclogermeselenanes $(Me_2GeSe)_n$ and a minor amount of the linear polymer $Cl(Me_2GeSe)_nCl$. Two years later $(Me_2GeSe)_3$ was synthesized again in Schmidt's^{445,446} laboratory. Its analogs and homologs $(R_2GeSe)_n$ as well as all the organylgermesquiselenanes $(RGeSe_{1.5})_n$ were not described until 1970.

In 1963, Ruidisch and Schmidt⁴⁴⁵ generated the first hexaalkyldigermeselenane $R_3GeSeGeR_3$, $R = Me$, together with Li_2Se by thermal decomposition at $>65^\circ C$ of $Me_3GeSeLi$. The precursor $Me_3GeSeLi$ was quantitatively produced by cleavage of $(Me_2GeSe)_n$ with methyllithium⁴⁴⁵ or by the action of selenium on Me_3GeLi ⁴⁴⁵. $Ph_3GeSeLi$ ^{247,436,442,443} was obtained similarly. $Me_3GeSeGeMe_3$ was also synthesized from $Me_3GeSeLi$ and Me_3GeCl ⁴⁴⁵. Lithium triethylgermaneselenolate was prepared by the reaction of Et_3GeSeH with Li in THF³⁶⁹ whereas the reaction of $MeMgI$ upon Et_3GeSeH resulted in $Et_3GeSeMgI$ ³⁶⁹. The reaction of the latter with Et_3GeBr gave $Et_3GeSeGeEt_3$ ³⁶⁹.

In 1965, $Ph_3GeSeGePh_3$ was synthesized in the same laboratory by reaction of $Ph_3GeSeLi$ with Ph_3GeBr ²⁴⁷. In 1966, Vyazankin and coworkers^{366–369} found that $Et_3GeSeGeEt_3$ was obtained in 22% yield upon heating Et_3GeH and Se at $200^\circ C$. It was suggested that Et_3GeSeH was an intermediate in the reaction and, indeed, it was obtained in 63% yield at $200^\circ C$ ^{367,368}. Heating Et_3GeSeH at $130^\circ C$ for a long time gave 37% of $Et_3GeSeGeEt_3$ ³⁶⁷. When trialkylgermanes R_3GeH reacted with Se at $200^\circ C$, R_3GeSeH ($R = i\text{-}Pr$, $c\text{-}C_6H_{11}$) were obtained in 67% and 31% yield, respectively⁴⁴⁷ together with the corresponding hexaorganoyldigermeselenanes $R_3GeSeGeR_3$. A more effective synthesis of $Et_3GeSeGeEt_3$ in 45% yield was the thermal ($200^\circ C$) reaction of Et_3GeSeH with Et_2Se ³⁶⁶. A convenient synthesis of hexaethyldigermeselenane was the reaction of $Et_3GeSeLi$ and Et_3GeBr ³⁶⁹. The reaction of Et_3GeSeH with Et_2Hg at $20^\circ C$ afforded $Et_3GeSeGeEt_3$ ³⁶⁹.

Triethyl(organylseleno)germanes Et_3GeSeR with $R = Bu$ ³⁶⁹, CH_2Ph ³⁶⁹, CH_2CH_2Ph ⁴⁴⁸ and CH_2CH_2COOEt ⁴⁴⁸ became known in 1967–1969. Compounds with $R = Bu$ and CH_2Ph were produced by the reaction of $Et_3GeSeLi$ with $BuBr$ and $PhCH_2Cl$. Unexpectedly, the reaction of $Et_3GeSeLi$ and 1,2-dibromoethane gave $Et_3GeSeGeEt_3$ and $CH_2=CH_2$ ³⁶⁹. Other compounds were prepared by hydroselenation (i.e. by photochemical addition of Et_3GeSeH to styrene and ethyl acrylate⁴⁴⁸). $Et_3GeSeBu$ was also synthesized

by the reaction of $(\text{Et}_3\text{Ge})_2\text{Hg}$ and BuSeH^{449} . Compounds having a Ge—Se—M group ($\text{M} = \text{Si}, \text{Sn}, \text{Pb}$) were first obtained in Schmidt's^{247,442,445,450} laboratory in 1963–1965. These were $\text{R}_3\text{GeSeMR}_3$, with $\text{M} = \text{Si}^{445}$, $\text{R} = \text{Me}$; $\text{M} = \text{Sn}^{247,442,450}$, Pb^{247} , $\text{R} = \text{Ph}$, and were produced by the reaction of the corresponding R_3GeSeLi and R_3MX ($\text{X} = \text{Cl}, \text{Br}$)²⁴⁷. $\text{Ph}_3\text{GeSeSnPh}_3$ was also synthesized, but with the 'opposite' reagents Ph_3GeBr with $\text{Ph}_3\text{SnSeLi}^{442,450}$. Finally, the Vyazankin group obtained $\text{Et}_3\text{GeSeGeEt}_3$ by the condensation of Et_3GeSeH with $\text{Et}_3\text{SnH}^{367}$ or of Et_3GeSeLi with $\text{Et}_3\text{SnCl}^{369}$.

In 1968, Mazerolles and coworkers⁴⁵¹ found that selenium inserted into the C—Ge bond of octaorganylgermacyclobutanes $\text{R}_2\text{Ge}(\text{CR}_2)_3$ gave octaorganyl-1-seleno-2-germacyclopentane.

The Vyazankin group studied some cleavage reactions of the Ge—Se bond. The reaction of $\text{Et}_3\text{GeSeGeEt}_3$ with bromine resulted in Et_3GeBr and Se, that with HCl led to Et_3GeCl and $\text{H}_2\text{Se}^{449}$ and, with sulfur, $\text{Et}_3\text{GeSGeEt}_3^{452}$ was formed.

Organogermanium compounds having Ge—Te bonds were also first prepared in Schmidt's and Vyazankin's laboratories in 1965–1967. Seven compounds [$\text{R}_3\text{GeTeGeR}_3$ ($\text{R} = \text{Et}, \text{Ph}, c\text{-C}_6\text{H}_{11}$), R_3GeTeR ($\text{R} = \text{Et}$) and $\text{R}_3\text{GeTeMR}_3$ ($\text{M} = \text{Si}, \text{Sn}, \text{Pb}$; $\text{R} = \text{Et}, \text{Ph}$)] were prepared in which the germanium atom was bound to the Group 14 element by the tellurium atom. Ph_3GeTeLi was synthesized along with these compounds by the reaction of Ph_3GeLi with tellurium in THF^{247,436,442,443}. The reaction of Ph_3GeTeLi with Ph_3GeBr , Ph_3SnCl and Ph_3PbCl gave the corresponding $\text{Ph}_3\text{GeTeMPh}_3$ ($\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$)²⁴⁷.

Hexaethyldigermtellurane was obtained by heating Et_3GeH either with tellurium at $190\text{--}210^\circ\text{C}^{447}$ or with diethyltelluride at $140^\circ\text{C}^{368,447}$ in 75% and 58% yields, respectively. It was synthesized by the reaction of Et_3GeH with $(\text{Et}_3\text{Si})_2\text{Te}^{452}$. Et_3GeTeEt was obtained for the first time (in 28–39% yield) by heating Et_3GeH with Et_2Te at $140^\circ\text{C}^{368,447}$. The reaction of Et_3GeTeEt with Et_3MH ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) at 20°C resulted in 60% $\text{Et}_3\text{GeTeMET}_3^{368,447}$. When $\text{Et}_3\text{GeTeGeEt}_3$ reacted with Et_3SnH at 170°C , Et_3GeH and $(\text{Et}_3\text{Sn})_2\text{Te}$ were produced³⁶⁸.

Vyazankin and coworkers⁴⁵² found that in the reaction of elementary S and Se with $\text{Et}_3\text{GeTeGeEt}_3$ the tellurium atom was replaced by the other chalcogen.

G. Organogermanium Pnicogen Derivatives

Among organogermanium derivatives in which the Ge atom is bound to Group 15 elements (pnictogens), the compounds having Ge—N bonds were the first to be studied.

The first compound of this family was tris(triphenylgermyl)amine $(\text{Ph}_3\text{Ge})_3\text{N}$, prepared by Kraus and Foster¹⁶¹ in 1927 by the reaction of Ph_3GeBr and liquid ammonia. In Kraus's laboratory^{197,198,224,370} all the triphenylgermylamines of the $(\text{Ph}_3\text{Ge})_n\text{NH}_{3-n}$ series, namely Ph_3GeNH_2 , $(\text{Ph}_3\text{Ge})_2\text{NH}$ and $(\text{Ph}_3\text{Ge})_3\text{N}$, were synthesized. The hydrolytically very unstable Ph_3GeNH_2 was produced by the reaction of gaseous ammonia and Ph_3GeBr in an inert solvent³⁷⁰. It was also synthesized by reaction of Ph_3GeBr and KNH_2 . With excess of KNH_2 the product was $\text{Ph}_3\text{GeNHK}^{370}$, which could be converted back to Ph_3GeNH_2 with NH_4Br . Kraus and coworkers found that Ph_3GeNH_2 was formed as a side product of the reaction of Ph_3GeNa with aryl halides¹⁹⁷ or methylene dihalides^{196,329} in liquid ammonia. They pointed out that by eliminating ammonia, Ph_3GeNH_2 could be condensed to the first representative of hexaorganyl digermazanes i.e. $\text{Ph}_3\text{GeNHGePh}_3^{370}$. When heating to 200°C , Ph_3GeNH_2 was entirely converted to $(\text{Ph}_3\text{Ge})_3\text{N}^{370}$.

In 1930 Kraus and Brown²²⁶ synthesized $(\text{Ph}_2\text{GeNH})_n$, $n = 3$ or 4 (although they considered the product to be 'diphenylgermanium imine' $\text{Ph}_2\text{Ge} = \text{NH}$), by the reaction of Ph_2GeCl_2 and liquid NH_3 . The compound was hydrolytically unstable.

The first hexaalkyldigermazane $\text{Et}_3\text{GeNHGeEt}_3$ was obtained in 1932 by Kraus and Flood¹⁴⁸ by reaction of Et_3GeBr with Na in liquid ammonia. Its hydrolysis gave hexaethyldigermoxane $\text{Et}_3\text{GeOGeEt}_3$. Ammonolysis of Et_2GeBr_2 gave $(\text{Et}_2\text{GeNH})_3$, which was hydrolyzed extremely easily to $(\text{Et}_2\text{GeO})_n$ ($n = 3, 4$)¹⁸⁸. Flood¹⁸⁸ in 1932, and much later Rijkens and van der Kerk^{76,77}, obtained $(\text{R}_2\text{GeNH})_3$, $\text{R} = \text{Et, Bu}$ by the reaction of Na in liquid ammonia with Et_2GeBr_2 and Bu_2GeCl_2 , respectively. In 1933, Flood³⁰⁶ found that during ammonolysis of EtGeX_3 ($\text{X} = \text{I, Br}$) a solid product corresponding to EtGeN , 'ethylgermanium nitride', was formed. Its hydrolysis resulted in polyethylgermesquioxane $(\text{Et}_3\text{GeO}_{1.5})_n$, 'ethylgermanic anhydride'. Therefore, Flood had prepared the first three-dimensional polyethylgermazane.

In 1931, Thomas and Southwood⁴⁵³ obtained pseudo-organic organyl- and diorganylamine derivatives of two- and four-valence germanium such as $\text{Ge}(\text{NHR})_2$ ($\text{R} = \text{Et, Ph}$), $\text{Ge}(\text{NEt}_2)_2$, $\text{Ge}(\text{NHPh})_4$ and $\text{Ge}(\text{NC}_5\text{H}_9\text{-}c)_4$.

Laubengayer and Reggel⁴⁵⁴, in 1943, synthesized $\text{Me}_3\text{GeNMe}_2$, the first organogermanium compound having a $\text{Ge}-\text{NR}_2$ group, by reacting Me_3GeCl and LiNMe_2 . Analogous compounds with $\text{R} = \text{SiMe}_3$ were produced much later from Me_3GeCl or Me_2GeCl_2 and $\text{NaN}(\text{SiMe}_3)_2$ ^{455,456}.

In 1952, Anderson⁴⁵⁷ synthesized a series of ethyl(dialkylamino)germanes $\text{EtGe}(\text{NR}_2)_3$ ($\text{R} = \text{Me, Et}$) by the direct reaction of EtGeCl_3 with dialkylamines. In 1949–1951 he discovered a new class of organogermanium compounds having $\text{Ge}-\text{N}$ bonds, the alkylisocyanatogermanes $\text{R}_{4-n}\text{Ge}(\text{NCO})_n$ ($\text{R} = \text{Et, Pr, } i\text{-Pr, Bu; } n = 1-3$). They were obtained from $\text{R}_{4-n}\text{GeCl}_n$ and AgNCO ^{314,315,387}. Rochow was an invisible participant in the work, since he gave Anderson Et_2GeCl_2 and EtGeCl_3 ³⁸⁷. In 1956, Anderson³⁷⁹ obtained $i\text{-Pr}_2\text{Ge}(\text{NCO})_2$ from the reaction of $i\text{-Pr}_2\text{GeCl}_2$ and AgNCO . Anderson hydrolyzed the alkylisocyanatogermanes, and their hydrolysis rates appeared to be the faster for the compounds with higher values of n . The cleavage of the $\text{Ge}-\text{N}$ bond in ethylisocyanatogermanes with alcohols $\text{R}'\text{OH}$ resulted in $\text{R}_{4-n}\text{Ge}(\text{OR}')_n$ ($\text{R} = \text{Me, Et, Bu; R}' = \text{Me, Et; } n = 1, 2$) and formation of H_2NCOOR ³⁸⁷. At the same time Anderson synthesized the first alkylisothiocyanatogermanes $\text{R}_{4-n}\text{Ge}(\text{NCS})_n$ ($\text{R} = \text{Et, Pr, Bu; } n = 2, 3$)^{184,376,379,458}. Compounds such as R_3GeNCS and $\text{R}_2\text{Ge}(\text{NCS})_2$, $\text{R} = \text{Et, Pr, Bu}$ were obtained in 1951 by cleavage of $\text{R}_3\text{GeOGeR}_3$ and $(\text{R}_2\text{GeO})_3$ with HNCS generated *in situ*³⁷⁶. Analogously, $i\text{-Pr}_2\text{Ge}(\text{NCS})_2$ was obtained from $(i\text{-Pr}_2\text{GeO})_3$. Exchange processes have also been studied, such as those of Et_3GeNCS with AgNCO and of Et_3GeCN with AgNCS ³⁷⁶.

It is remarkable that the rather intensive investigations on nitrogen-containing organogermanium compounds during a quarter of a century were followed by reduced activity. From 1952 till 1963 they were mentioned only in seven publications^{184,328,337,381,458-460}, five of which devoted to compounds having the $\text{Ge}-\text{NCY}$ bond ($\text{Y} = \text{O, S}$). No new compounds having the digermazane group ($\text{Ge}-\text{N}-\text{Ge}$) have been reported during this period.

The activity in the field was then resumed. In 1963, Onyszchuk³³¹ carried out the reaction of Me_3GeBr , Et_2GeCl_2 and Ph_2GeCl_2 with liquid ammonia at -78°C which gave the 1 : 1 adducts. On raising the temperature the products were converted to the corresponding ammonolysis products $[\text{Me}_3\text{GeNH}_3]^+\text{Br}^-$ and $(\text{R}_2\text{GeNH})_n$ ($n = 2, 3$).

In 1964, Ruidisch and Schmidt⁴⁶¹ synthesized hexamethyldigermazane by the reaction of Me_3GeCl and gaseous NH_3 in diethyl ether. At -60°C a considerable quantity of $(\text{Me}_3\text{Ge})_3\text{N}$ ⁴⁶² was formed. In the same year the authors also obtained organogermanium azides $\text{Me}_{4-n}\text{Ge}(\text{N}_3)_n$ ($n = 1, 2$) by reacting $\text{Me}_{4-n}\text{GeCl}_n$ and NaN_3 ⁴⁶³. At the same time Thayer and West⁴⁶⁴ as well as Reichle⁴⁶⁵ synthesized Ph_3GeN_3 from Ph_3GeBr .

In 1964, Rijkens and van der Kerk⁷⁷ obtained hexabutylcyclotrigermazane $(\text{Bu}_2\text{GeNH})_3$ by the reaction of Bu_2GeCl_2 with a Na solution in liquid NH_3 .

In 1964–1966, Satge and coworkers^{36,37} used reactions of alkylhalogermanes with amino lithium and organomagnesium derivatives to generate Ge–N bonds.

Satge and Baudet⁴⁶² synthesized in 1966 hexaethyldigermazane by the reaction of Et_3GeCl and LiNH_2 in THF. The extremely unstable Et_3GeNH_2 was a probable intermediate in the reaction.

At the same year Massol and Satge³⁵⁶ discovered that the ammonolysis of $\text{Et}_{3-n}\text{GeH}_n\text{Cl}$ ($n = 1, 2$) led to the corresponding trigermylamines ($\text{Et}_{3-n}\text{GeH}_n$)₃N (when $n = 1$, $\text{Et}_2\text{GeHNHGeHEt}_2$ was also formed). By contrast, Et_3GeCl ($n = 0$) did not give $(\text{Et}_3\text{Ge})_3\text{N}$ on reaction with ammonia. That indicated a steric effect of the $\text{R}_{3-n}\text{GeH}_n$ group on the chlorides during ammonolysis. Accordingly $\text{Me}_3\text{GeNMe}_2$, which has less bulky substituents than Et_3Ge , underwent ammonolysis to give $(\text{Me}_3\text{Ge})_3\text{N}$. The latter was formed also by the reaction of Me_3GeCl and $\text{Li}(\text{GMe}_3)_2$ or LiN_3 ⁴⁶² as well as by the reaction of MeLi and $(\text{ClMe}_2\text{Ge})_3\text{N}$ ⁴⁶¹.

According to Wieber and Schwarzmann⁴³⁴, ammonolysis of $\text{ClCH}_2\text{Me}_2\text{GeCl}$ resulted in $\text{ClCH}_2\text{Me}_2\text{GeNHGeMe}_2\text{CH}_2\text{Cl}$, the first carbon functionalized hexaalkyldigermazane derivative.

In 1964–1965, Rijkens and coworkers synthesized a series of nitrogen heterocycles (pyrrole, pyrazole, imidazole, triazole, succinimide, phthalimide), N-triorganylgermyl derivatives, and studied their properties^{76,466}.

In 1969, Highsmith and Sisler⁴⁶⁷ attempted to repeat the reaction of Ph_3GeBr and ammonia, described by Kraus and Foster¹⁶¹, but they obtained only $\text{Ph}_3\text{GeNHGePh}_3$ instead of $(\text{Ph}_3\text{Ge})_3\text{N}$.

Since the first synthesis of organogermanium nitrogen derivatives it was found that the Ge–N bonds display high reactivity, especially an easy protolysis with water, alcohols, phenols, carboxylic acids, hydrohalic acids, SH-, NH-, PH- and CH-acids, etc.^{36,37,77,346,347}. All these reactions were initiated by electrophilic attack of the reactant proton on the nitrogen atom^{76,468,469}.

In particular, Anderson⁴⁵⁷ in 1952 found out that the Ge–N bond in $\text{EtGe}(\text{NMe}_2)_3$ was cleaved by HI to give EtGeI_3 . From 1964 ammonolysis^{76,347}, aminolysis³⁴⁷, amidolysis³⁴⁷ and hydrazinolysis⁴⁷⁰ reactions of trialkyl(dimethylamino)germanes R_3GeNMe_2 ($\text{R} = \text{Me}, \text{Et}$) resulting in $\text{R}_3\text{GeNHGeR}_3$, $\text{R}_3\text{GeNHR}'$, $\text{R}_3\text{GeNHCOR}'$ and $\text{R}_3\text{GeNHNHR}'$, respectively, were discovered.

Under strict reaction conditions (sometimes in the presence of $(\text{NH}_4)_2\text{SO}_4$) peralkylgermazanes $(\text{R}_3\text{Ge})_n\text{NH}_{3-n}$ ^{76,462} ($n = 2, 3$) were cleaved.

Schmidt and Ruidisch⁴⁷¹ in 1964 were the first to cleave the Ge–N–Ge group with organometallic reagents in the reaction of $(\text{Me}_2\text{GeNMe})_3$ and MeLi , which gave $\text{Me}_3\text{GeN}(\text{Li})\text{Me}$.

In 1964–1969, cleavage reactions of the Ge–N bond by anhydrides, carboxylic acids chloroanhydrides³⁴⁷, chloramine⁴⁷², metal halides⁴⁷³, and trimethylchlorometalanes Me_3MCl ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) were described.

The addition reactions of trialkyl(dimethylamino)germanes to activated double and triple bonds were discovered in 1967–1968^{474,475}.

The first investigations of Satge and coworkers on the introduction of organic and inorganic compounds having $\text{M}=\text{Y}$ groups⁴⁷⁰ (CO_2 , CS_2 ³⁴⁷, PhNCO , PhNCS ⁴⁷⁶, F_3CCOCF_3 ⁴⁷⁷) into the Ge–N bond are of particular interest. Glockling and Hooton⁴⁷⁸ were the first to obtain in 1963 organogermanium compounds having Ge–P bonds (e.g. $\text{Et}_3\text{GePPh}_2$) by reaction of Et_3GeBr with Ph_2PLi . A year later Satge and coworkers^{347,462} synthesized the same compound by cleavage of $\text{Et}_3\text{GeNMe}_2$ with diphenylphosphine.

In 1969, Schumann-Ruidisch and Kuhlmeier⁴⁷⁹ carried out analogous reactions of $\text{Me}_3\text{GeNMe}_2$ with RPH_2 ($\text{R} = \text{Me}, \text{Ph}$), which resulted in $(\text{Me}_3\text{Ge})_2\text{PR}$ and Me_3GePHPh .

Norman⁴⁸⁰ proposed a new approach to the synthesis of compounds R_3GePH_2 by reaction of R_3GeCl with $LiAl(PH_2)_4$.

In 1965, Brooks and coworkers⁴⁸¹ discovered that the reaction of $Ph_{4-n}GeBr_n$ ($n = 2, 3$) and Ph_2PLi afforded $Ph_{4-n}Ge(PPh_2)_n$. Satge and Couret⁴⁷⁴ similarly synthesized Et_3GePEt_2 from Et_3GeCl and Et_2PLi .

In 1965–1966, Schumann and coworkers^{482,483} carried out the condensation of Ph_3GeCl with PH_3 and $PhPH_2$, which led to $(Ph_3Ge)_3P$ and $(Ph_3Ge)_2PPh$, respectively. Ph_3GeOH ⁴⁸³ was formed by cleavage of these compounds by an alcoholic KOH solution. $(Me_3Ge)_3P$ ⁴⁸⁴ was synthesized by the reaction of Me_3GeNMe_2 with PH_3 .

The Ge–P bond turned out to be extremely active. For example, $R_3GePR'_2$ ($R = R' = Et, Ph$) was easily cleaved by water, alcohols, carboxylic acids, HCl, HBr, thiols, aniline and ammonia^{474,481,485}. Oxidation of Et_3GePPh_2 by oxygen involved insertion into the Ge–P bond as well and resulted in $Et_3GeOPOPh_2$. The latter was also produced in the reaction of $Et_3GeOGeEt_3$ and Ph_2POOH ⁴⁸¹. When Et_3GePPh_2 reacted with bromine, Et_3GeBr and Ph_2PBr were formed. Butyllithium cleavage of Et_3GePPh_2 led to Et_3GeBu and Ph_2PLi . It is noteworthy that the Ge–P bond in Et_3GePPh_2 was cleaved even by methyl iodine to give Et_3GeI and Ph_2PMe . The reaction of Ph_2PMe and excess of MeI gave $[Me_2Ph_2P]^+I^-$ ^{347,481}. When Et_3GePPh_2 and AgI were added to the reaction mixture, the complex $[Et_3GePPh_2 \cdot AgI]_4$ ⁴⁸¹ was produced.

CS_2 , $PhNCS$, $PhNCO$, $PrCHO$, $PhCHO$, $CH_2=C=O$, $CH_2=CHCN$ and $PhC\equiv CH$ ^{474,486,487} insert into the Ge–P bond of Et_3GePR_2 ($R = Et, Ph$) similarly to their insertion into the Ge–N bond. Et_3GePEt_2 added to α,β -unsaturated aldehydes at the 1,4-positions⁴⁸⁶.

There was only one report before 1970 on organogermanium arsenic derivatives. In 1966, Schumann and Blass⁴⁸⁴ prepared $(Me_3Ge)_3As$ by the reaction of Me_3GeNMe_2 with AsH_3 and described some of its properties.

H. Compounds having a Hypovalent and Hypervalent Germanium Atom

The formation of inorganic compounds of hypovalent (divalent) germanium such as dihalo germanium GeX_2 (i.e. dihalogermynes) was already noted by Winkler^{16,23} in the 19th century. He reported the existence of $GeCl_2$ in HCl solution and of GeF_2 as the reduction product of K_2GeF_6 by hydrogen. However, only in the beginning of the 20th century did fundamental investigations of dihalo germanium, including monomeric GeX_2 , start^{77,488–491}.

In 1926–1934, some methods for the gas-phase generation of monomeric inorganic derivatives of divalent germanium such as H_2Ge ^{332,492}, F_2Ge ^{493,494}, Cl_2Ge ^{495,496} and Br_2Ge ⁴⁹⁷ were developed. Dennis and Hance⁴⁹⁸ obtained solid GeI_2 for the first time in 1922. It turned out not to be a monomer, since the germanium atom was surrounded octahedrally with six iodine atoms⁴⁹⁹ in its crystal lattice. However, at a high temperature GeI_2 dissociated to form the monomeric molecules.

Interesting complexes of GeI_2 and CH_3NH_2 ⁵⁰⁰ or Me_4NI have been described. The reaction of GeI_2 with NH_3 gave germanium(II) imide $Ge=NH$, which could be hydrolyzed to $Ge(OH)_2$, i.e. $(H_2O \cdot GeO)$ and NH_3 ⁵⁰¹. Complexes of GeF_2 with Et_2O and with Me_2SO ⁵⁰² were described in 1960–1962 and series of complexes of GeF_2 ⁵⁰³, $GeCl_2$ ⁵⁰⁴ and $GeBr_2$ ^{505,506} were obtained as well. Thus, the inorganic chemistry of germynes was born almost simultaneously with their organogermanium chemistry.

Organogermanium derivatives R_2Ge , which are often regarded as monomers, proved to be cyclic oligomers or linear polymers. The first attempt to synthesize monomeric diorganylgermylenes was made by Kraus and Brown¹⁹⁸. In 1930 they tried to obtain diphenylgermylene by reduction of Ph_2GeCl_2 with sodium metal in boiling xylene, but

the product was a mixture of cyclic oligomers $(\text{Ph}_2\text{Ge})_n$. Only in 1963 did Neumann and Kühlein¹⁹⁹ determine that the main product of the reaction was octaphenylcyclotetragermane $(\text{Ph}_2\text{Ge})_4$, i.e. a tetravalent germanium derivative.

In the 1960s, Nefedov, and his coworkers, Kolesnikov^{201–207,507}, Neumann and coworkers^{175,199,200,508,509}, Glockling and Hooton²⁴⁹ and other investigators^{36,37,69,77,185,210,239,240,490,510,511} started to study the generation of diorganylgermylenes. However, the reduction reactions of diorganyldihalogermanes by alkali metals, as well as the reaction of dihalogermanes with organometallic compounds (cf. Section II.B.) always resulted in the formation of cyclic oligomers, linear polymers or the insertion products of the R_2Ge moiety into bonds of the solvents or the reagents. For example, in 1954 Jacobs²⁴⁰ tried to produce dialkylgermylenes by reaction of GeI_2 with a series of organometallic compounds (EtLi , BuLi , Bu_2Zn , Et_2Hg , Bu_2Hg). However, the only organogermanium compound that he was able to isolate was $\text{IBu}_2\text{GeGeBu}_2\text{I}$. The latter was also formed along with metallic mercury in the reaction of GeI_2 and Bu_2Hg .

In spite of these failures, all the authors had no doubts that diorganylgermylenes were the intermediates in the reactions studied.

Nefedov and coworkers^{204,207,507} confirmed the generation of dimethylgermylene Me_2Ge in the reaction of Me_2GeCl_2 and Li based on the fact that its addition product to ethylene was formed. According to Vyazankin and coworkers⁵¹² diethylgermylene was evidently an intermediate in the thermal (200°C) decomposition of $\text{Et}_3\text{GeGeEt}_3$ with AlCl_3 catalyst which resulted in $(\text{Et}_2\text{Ge})_n$ and Et_4Ge . In 1966, Bulten and Noltes⁵¹³ observed an analogous decomposition of $\text{ClEt}_2\text{GeGeEt}_2\text{Cl}$ and $\text{Et}_3\text{GeGeEt}_2\text{Cl}$. In both cases one of the products obtained was $(\text{Et}_2\text{Ge})_n$, formed along with Et_2GeCl_2 or Et_3GeCl , respectively. The intermediate generation of Et_2Ge was confirmed by its insertion into the $\text{Ge}-\text{Cl}$ bond of the precursor chloride with the formation of oligomers such as $\text{Et}_3\text{Ge}(\text{Et}_2\text{Ge})_n\text{Cl}$ ($n = 1, 2$).

Neumann and Kühlein^{175,199,509} found in 1963 another precursor of diorganylgermylenes, the organomercurygermanium polymer $(-\text{Ph}_2\text{Ge}-\text{Hg}-)_n$, which was synthesized by the reaction of Ph_2GeH_2 and Et_2Hg . Unfortunately, in the early 1960s the Neumann laboratory did not have available spectroscopic techniques for the identification of the highly reactive short-lived diorganylgermylenes and other labile intermediates.

Nefedov and coworkers²⁰² had proven in their first publication that Me_2Ge was the intermediate formed in the reaction of Me_2GeCl_2 and Li , since when the reaction was conducted in the presence of styrene, 1,1-dimethyl-3,4-diphenyl-1-germacyclopentane was formed in 40% yield.

The possibility of thermal generation of diorganylgermylene was established for the first time at the Nefedov laboratory in 1964–1965^{203,205,207,507}. Thermolysis of $(\text{Me}_2\text{Ge})_n$ where n is ca 55 at $350\text{--}400^\circ\text{C}$ led to Me_2Ge which was identified by its addition products to tolan and ethylene, together with its dimeric and polymeric biradicals²⁰⁷ and to $(\text{Me}_2\text{Ge})_n$ ($n = 6, 5$ and 4) as well. Shorigin, Nefedov and coworkers²⁰⁶ were the first to obtain the UV spectra of polydiorganylgermylenes $(\text{Me}_2\text{Ge})_n$.

The publications of Glockling and Hooton²⁴⁹ and of Summers²³⁹ were of special interest, because they reported the formation of diphenylgermylene from Ph_2GeHOMe by α -elimination of methanol. This led to the conclusion that the intermediate products in the formation of R_2Ge from R_2GeX_2 or GeX_2 ($\text{X} = \text{halogen}$) were $\text{R}_2\text{Ge}(\text{X})\text{M}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{MgX}$), which further decomposed to MX by an α -elimination process.

It was surprising that Neumann did not investigate the thermal and photochemical reactions of the decomposition of $(\text{Ph}_2\text{Ge})_n$.

Cited as follows, publications of Nefedov and Kolesnikov^{201–207,507}, Neumann^{175,199,200,508,509} and their coworkers can be regarded as the beginning of the chemistry of diorganylgermylenes.

Entrapping and subsequent investigations of diorganylgermylenes in hydrocarbon or argon matrices were carried out only in the 1980s^{491,508}. Metlesics and Zeiss²¹¹ showed the possible existence of organylhalogermynes. They considered PhClGe : to be the intermediate formed in the reaction of PhGeCl_3 and Li amalgam.

Kinetically stable diorganylgermylenes $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Ge}$ and $[2,4,6-(\text{Me}_3\text{C})_3\text{C}_6\text{H}_8\text{-}c]_2\text{Ge}$ ^{491,514,515} were obtained and described in the last quarter of the 20th century. Different transformations of diorganylgermylenes (especially their insertion and dimerization reactions^{69,508,510,516}) were studied in the 1980s. New precursors of diorganylgermylenes such as 7,7-diorganyl-7-germabenzonorborenes, $\text{Ar}_2\text{Ge}(\text{SiMe}_3)_2$, $\text{Me}_2\text{Ge}(\text{N}_3)_2$, and some heterocyclic compounds having endocyclic Ge—Ge⁵⁰⁸ bonds were discovered at that very time, but we cannot dwell on these investigations in more detail.

Short-lived Ge-centered free radicals of $\text{R}_3\text{Ge}^\bullet$ belong to the hypovalent (trivalent) germanium derivatives. In 1953–1957, Gilman and coworkers^{195,217,219,229,517,518}, based on the dissociation of hexaphenylethane to free $\text{Ph}_3\text{C}^\bullet$ radicals, tried to obtain the $\text{Ph}_3\text{Ge}^\bullet$ radical by dissociation of $\text{Ph}_3\text{GeMPh}_3$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$).

The stability of the Ge—Ge bond in $\text{Ph}_3\text{GeGePh}_3$ to homolytic cleavage to $\text{Ph}_3\text{Ge}^\bullet$ radicals was evidenced from the fact that the compound melted at 336°C without decomposition²⁴⁹. Hexaethyldigermene was thermally stable as well and could be distilled under atmospheric pressure at 265°C ¹⁴⁸.

The results of thermal decomposition of polydimethylgermylenes $(\text{Me}_2\text{Ge})_n$ ²⁰⁵ ($n \geq 2$) provide evidence in favor of the formation of Ge-centered biradicals $^\bullet(\text{Me}_2\text{Ge})_n^\bullet$. It is suggested that the initial step of the thermal decomposition ($>400^\circ\text{C}$) of tetraalkylgermanes R_4Ge ($\text{R} = \text{Me}, \text{Et}$), which are widely used in producing germanium films^{151,152}, involves the formation of free radicals $\text{R}_3\text{Ge}^\bullet$. We note that Gaddes and Mack⁵¹⁹ in 1930 were the first to carry out thermal cleavage of Et_4Ge starting at *ca* 420°C . The final cleavage products seemed to be Ge and C_4H_{10} . It is very likely that the data on Ge-centered organogermanium free radicals reviewed in the period under discussion are limited to what was reported in the references mentioned above.

Compounds $\text{R}_2\text{Ge}=\text{Y}$ ($\text{Y} = \text{GeR}_2, \text{CR}_2, \text{NR}', \text{O}, \text{S}$), in which the Ge atom is three-coordinated and is bonded by a $\pi(\text{p-p})$ bond with a Ge atom or with another element, can be considered as hypovalent germanium derivatives. The simplest concept of germanium atoms binding in the $\text{R}_2\text{Ge}=\text{GeR}_2$ molecule can be presented in the following way: $\text{R}_2\ddot{\text{Ge}}-\ddot{\text{Ge}}\text{R}_2$ ^{514,516}.

Information about compounds having Ge=Y bonds were published much later than the period considered above of organogermanium chemistry evolution. We only refer to some pertinent reviews^{491,520–523}.

Hypervalent germanium derivatives are compounds having penta-, hexa- and sometimes heptacoordinate germanium atom. Numerous publications are devoted to inorganic and pseudo-organic (with no C—Ge bonds) derivatives of this type^{159,488,518,524–528}.

Of particular interest are pseudo-organic compounds of hypervalent germanium such as germanium tetrahalide complexes with amines, complexes of GeX_4 with β -diketones^{159,527}, polyatomic alcohols and phenols^{159,488,524}, phthalocyanines¹⁵⁹, and others. The first labile hypervalent organogermanium compound $\text{Ph}_3\text{Ge}(\text{NH}_3)_3\text{Na}$ was obtained by Kraus and Foster¹⁶¹ by cleavage of $\text{Ph}_3\text{GeGePh}_3$ with sodium in liquid ammonia.

The formation of organic derivatives of penta- and hexacoordinate germanium is due to a later time when the reactions of organohalogermenes were studied with ammonia and amines (see Section II.F). When these reactions were conducted at low temperatures, 1 : 1 and 1 : 2 adducts were formed. When heated $>0^\circ\text{C}$, the complexes of organohalogermenes with ammonia, primary and secondary amines decomposed to give compounds

with a Ge–N bond and quaternary ammonium salts³³¹. Such reactions were described for the first time in 1926–1933^{148,188,453,457,529–533}. However, Kraus and Flood¹⁴⁸ found that the only reaction product of Et_3GeBr and liquid ammonia was the monoadduct $[\text{Et}_3\text{GeNH}_3]^+\text{Br}^-$ ⁷⁵. Organohalogermanes and tertiary amines formed rather stable 1 : 1 or 1 : 2 complexes, which were unstable toward hydrolysis.

Sowa and Kenny⁵³⁴ in 1952 patented the unusual complex compounds $[\text{R}_{4-n}\text{Ge}(\text{N}^+\text{R}'_3)_n]\text{X}^-$ ($n = 1-4$) obtained from $\text{R}_{4-n}\text{GeX}_n$ and tertiary amines.

The first stable intramolecular complexes of pentacoordinate organogermanium derivatives (1-organylgermatranes $\text{RGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$) having a transannular $\text{Ge} \leftarrow \text{N}$ bond were synthesized in the Voronkov laboratory in 1965³⁹⁷. Their synthesis was based on the direct use of RGeCl_3 and $(\text{RGeO}_{1.5})_n$ ^{397,398}. Their molecular and crystalline structure^{83,535,536}, UV spectra⁵³⁷, ^1H ⁵³⁸, ^{13}C ⁵³⁹ and ^{15}N ⁵⁴⁰ NMR spectra as well as their biological activity^{398,541–543} have been investigated. Mironov, Gar and coworkers^{82,84} later contributed to the investigations of germatranes and their biological activity.

Beginning from 1989, another interesting series of intramolecular organogermane complexes, such as Ge-substituted N-germylmethylactames, were investigated extensively by Baukov, Pestunovich, Voronkov, Struchkov and others^{544,545}.

I. Biological Activity

The biological activity of germanium compounds and their influence on the biosphere have been considered in detail in an excellent monograph of Latvian and Russian chemists published in 1990 (in which 767 references are cited⁸⁶) as well as in earlier reviews by the same authors^{82,546–548}.

Investigations of the effect of inorganic germanium compounds on living organisms began in 1922 when it was discovered that germanium dioxide stimulated erythropoiesis (production of red blood cells). In the same year the toxicity of GeO_2 was determined for the first time^{549–553}. The results of germanium dioxide toxicological studies were published in 1931–1944^{553–556}. The growing interest in the chemistry of germanium, especially in the middle of the 20th century, led to numerous investigations of the biological activity of inorganic compounds of this element (GeO_2 , RGeOOH and its salts, metal hexafluorogermanates, GeH_4 , GeCl_4 , GeF_4 , GeS_2), which were undertaken mostly after 1953^{48,75,86}.

Even in the first half of the last century it was already established that many organogermanium compounds did not suppress *Trypanosoma*, *Spirochaeta*, *Pneumococcus*, *Streptococcus*^{557,558} and test rat sarcoma⁵⁵⁹. Moreover, in 1935 Carpenter and coworkers⁵⁶⁰ found that $(\text{Me}_2\text{GeO})_n$ stimulated the growth of many kinds of microorganisms. Much later, Rochow and Sindler⁵⁶¹ found that $(\text{Me}_2\text{GeO})_4$ did not show either toxic or irritating action on mammals (hamsters, rabbits). However, this oligomer exerted a teratogenic effect on chicken embryos and was more toxic to them than acetone^{476,562}. The toxicity of $(\text{R}_2\text{GeO})_n$ ($\text{R} = \text{Me}, \text{Et}, \text{Bu}; n = 3, 4$) was determined by Rijkens and van der Kerk⁷⁶ and by Caujiolle and coworkers⁵⁶³ in 1964–1966.

In 1936, Rothermundt and Burschkies⁵⁵⁷ tried to establish the possibility of chemotherapeutic use of organogermanium compounds. They determined the toxicity of many types of substances such as R_4Ge , R_3GeX , R_3GeGeR_3 , $(\text{RGeO}_{1.5})_n$ and $(\text{ReGeS}_{1.5})_n$, where $\text{R} = \text{alkyl}, \text{cyclohexyl}, \text{aryl or benzyl}$. The conclusion reached was that organogermanes are of moderate therapeutic use because of their total low toxicity. In another article Burschkies⁴³¹ has reported that these compounds are of no chemotherapeutic use. Nevertheless, Rijkens and coworkers^{75,564} thought that this statement was premature.

In 1962, Kaars⁵⁶⁴ first investigated the fungicidal activity of trialkyl(acetoxy)germanes. In contrast to analogous tin and lead derivatives, they were inactive. Triethyl(acetoxy)germane appeared to be considerably less toxic to rats (LD_{50} 125–250 mg kg⁻¹ *per-os*) than isostructural tin and lead compounds. Its homologs, $R_3GeOOCMe$ ($R = Pr, Bu$), did not show any toxic action⁵⁶⁵. In general, no specific biological activity of compounds of type $R_3GeOOCMe$ has been found. The toxicity of alkylhalogermanes $Bu_{4-n}GeCl_n$ ($n = 0-3$) or $RGeI_3$ ($R = Me, Et, Pr$) was within a range of 50–1300 mg kg⁻¹⁵⁶⁶ on intraperitoneal administration.

The toxicity of hexaalkyldigermoxanes $R_3GeOGeR_3$ ($R = Me-Hex$)^{76,567} was determined in 1963–1964.

Italian pharmacologists in 1963–1966 studied extensively the toxicity of tetraalkylgermanes. All the compounds were practically nontoxic (LD_{50} 2300–8100 mg kg⁻¹), except *i*- Pr_4Ge (LD_{50} 620 mg kg⁻¹). It is noteworthy that the toxicity of $Et_3GeCH_2CH=CH_2$ (LD_{50} 114 mg kg⁻¹) was 40 times lower than that of its saturated analog Et_3GePr .

In 1969, diphenyl(iminodiacetoxy)germane was recommended for use as an insecticide⁵⁶⁸. The lower toxicity of organic germanium compounds compared to that of isostructural silicon compounds was reasonably confirmed by Voronkov and coworkers^{398,569} in 1968; they found that 1-phenylgermatrane was 100 times less toxic than 1-phenylsilatrane (LD_{50} 0.3–0.4 and 40 mg kg⁻¹, respectively), although it showed an analogous physiological action.

Nevertheless, $PhGe(OCH_2CH_2)_3N$ was not the most toxic organogermanium derivative. Toxicological investigations in 1979 with other 1-organylgermatranes $RGe(OCH_2CH_2)_3N$ ^{84,86} showed that most of them had low toxicity (LD_{50} 1300–10000 mg kg⁻¹). Compounds with $R = H$ and $BrCH_2$ showed LD_{50} of 320 and 355 mg kg⁻¹, respectively⁸⁶. The most toxic compounds were 1-(2-thienyl)germatrane and 1-(5-bromo-2-thienyl)germatrane (LD_{50} 16.5 and 21 mg kg⁻¹, respectively). Nevertheless, their toxicity was 10–12 times lower than that of 1-(2-thienyl)silatrane (LD_{50} 1.7 mg kg⁻¹)⁵⁷⁰. It is remarkable that 1-(3-thienyl)germatrane was several times less toxic (LD_{50} 89 mg kg⁻¹) than that of its isomer mentioned above.

The discovery of a wide spectrum of biological activity of the organogermanium drug Ge-132 has stimulated extensive investigations in the field of synthesis and pharmacology of carbofunctional polyorganylgermsesquioxanes $(RGeO_{1.5})_n$. For this purpose Asai established a special Germanium Research Institute and a clinic^{81,571} in Tokyo. It should be mentioned that a cytotoxic antitumor drug 2-(3-dimethylaminopropyl)-8,8-diethyl-2-aza-8-germaspiro[4,5]decane, 'spirogermany'^{572,573}, was developed in 1974.

Further events in bio-organogermanium chemistry, which was born soon after bio-organosilicon chemistry^{547,548}, have been described in a monograph⁸⁶.

The practical application of organogermanium compounds has been developed since the last quarter of the 20th century. They were used in medicine and agriculture as drugs and biostimulants^{86,574} as well as in the microelectronic industry to produce thin films of elementary germanium^{151,152}.

III. ORGANOTIN COMPOUNDS

A. How it All Began

The chemistry of organotin compounds was born in the middle of the 19th century almost simultaneously with the birth of the chemistry of organolead compounds. Organic derivatives of these two Group 14 elements started to develop three quarters of a century earlier than those of germanium, their neighbor in the Periodic Table. Due to this large

age difference, the review of the evolution of organotin compounds will cover a period of only 110 years, up to the beginning of the 1960s.

Carl Jacob Löwig (1803–1890), a professor at Zürich University, laid the foundation for the chemistry of organotin compounds. He is honored by the synthesis of the first organic compounds of tin in 1852⁴¹. Polydiethylstannylene (Et_2Sn)_n was obtained in his unpretentious laboratory before other organotin compounds by the reaction of ethyl iodide with an alloy of tin containing 14% of sodium (he found that the optimal Sn:Na ratio is 6 : 1). Triethyliodostannane and hexaethyldistannane were formed together with it. At a later date it was discovered that another reaction product was tetraethylstannane^{575,576}. Consequently, Löwig^{41,577–582} became the founder of the direct synthesis of organotin compounds. During his investigations he observed that the polydiethylstannylene obtained was easily oxidized in air to a white precipitate, which by modern concepts is a mixture of perethyloligocyclostannoxanes (Et_2SnO)_n. The latter was prepared by the reaction of Et_2SnI_2 with Ag_2O or with aqueous ammonia. Löwig found that the action of alcoholic HCl solution on (Et_2SnO)_n led to Et_2SnCl_2 . By the reaction of a solution of KOH saturated with hydrogen sulfide with Et_2SnCl_2 , Löwig obtained oligodiethylcyclostannathianes (Et_2SnS)_n as an amorphous precipitate having a penetrating foul smell. However, all the other compounds obtained had not quite a sweet smell, and they irritated the eyes and mucous membranes.

The reaction of Et_2Sn with bromine and chlorine (with iodine, a fire was created) resulted in the corresponding Et_2SnX_2 ($\text{X} = \text{Cl}, \text{Br}$). When Et_2Sn reacted with HCl, Et_2SnCl_2 was also formed⁴¹.

Triethyliodostannane was converted to hexaethyldistannoxane by treatment with aqueous ammonia, and hexaethyldistannoxane was converted to triethylchlorostannane by reaction with HCl.

Löwig⁴¹ and then Cahours⁵⁸³ obtained diethylstannyldinitrate $\text{Et}_2\text{Sn}(\text{ONO}_2)_2$ and triethylstannylnitrate $\text{Et}_3\text{SnONO}_2$ ^{41,584}, by the reaction of HNO_3 with Et_2SnO and $\text{Et}_3\text{SnOSnEt}_3$, respectively. The reaction of diethyliodostannane with Ag_2SO_4 gave diethylstannylenesulfate $\text{Et}_2\text{SnO}_2\text{SO}_2$ ^{41,583,585}.

In spite of the rather tedious investigations of Löwig which were conducted at the level of 19th century chemistry, they resulted both in syntheses and the study of reactivities of the first organotin compounds. He interpreted his results by the then predominant theory of radicals and used the obsolete values of 6 and 59, respectively, for the carbon and tin atomic weights.

Though a very experienced detective is required to investigate the Löwig publications, it is clear that Löwig had in his hands the first representatives of the main classes of the organotin compounds, i.e. (R_2Sn)_n, R_3SnSnR_3 , (R_2SnO)_n, $\text{R}_3\text{SnOSnR}_3$, R_3SnX , R_2SnX_2 , as their ethyl derivatives. It is rather interesting to compare the Löwig formulas and names for his organotin compounds with the modern ones (Table 2).

It is regretful that the Löwig papers devoted to organotin compounds were published only during one year^{41,577–579,586}. He then stopped the investigations in this field. Evidently, this was caused by his leaving Zürich for Breslau, where he was invited to take Bunsen's position.

Bunsen, who accepted the chair in Heidelberg University, left his new laboratory in Breslau to his successor. Löwig's termination of his organotin investigations possibly reflects his unwillingness to impose severe hazards upon himself and the people surrounding him by the poisoning and irritating vapors of the organotin and organolead compounds to which he was exposed in Zürich. Nevertheless, Löwig did not forget the organic tin and lead compounds and his publications^{43,587}, where he did not fail to mention his priority and which are part of the history of organometallic compounds^{579–582}, bear witness to this fact.

TABLE 2. Names and formulas of organotin compounds synthesized by Löwig

| Modern formula | Löwig's formula | Löwig's name (<i>in German</i>) |
|--|--|-------------------------------------|
| $\text{Et}_3\text{SnSnEt}_3$ | $\text{Sn}_4(\text{C}_4\text{H}_5)_3$ | Acetstannäthyl |
| Et_4Sn | $\text{Sn}_4(\text{C}_4\text{H}_5)_5$ | Äethstannäthyl |
| Et_3SnOEt | | Acetstannäthyl-oxyd |
| Et_2SnCl_2 | | Chlor-Elaylstannäthyl |
| Et_2SnBr_2 | | Brom-Elaylstannäthyl |
| Et_2SnI_2 | | Iod-Elaylstannäthyl |
| $(\text{Et}_2\text{SnO})_n$ | Et_2SnO | Elaylstannäthyl-oxyd |
| $\text{Et}_3\text{SnOSnEt}_3$ | | Methylenstannäthyl-oxyd |
| $\text{Me}_3\text{SnONO}_2$ | $\text{Sn}_2(\text{C}_4\text{H}_5)_3\text{O}, \text{NO}_5$ | Salpetersäure Methstannäthyl-oxyd |
| $\text{Et}_3\text{SnONO}_2$ | $\text{Sn}_4(\text{C}_4\text{H}_5)_4\text{O}, \text{NO}_5$ | Salpetersäures Elaylstannäthyl-oxyd |
| $(\text{Et}_3\text{SnO})_2\text{SO}_2$ | $\text{Sn}_2(\text{C}_4\text{H}_5)_3\text{O}, \text{SO}_3$ | Schwefelsäure Methstannäthyl-oxyd |
| $\text{Et}_3\text{SnONO}_2$ | | Salpetersäure Acetstannäthyl-oxyd |

In spite of Löwig's outstanding research, which laid the foundation of organotin chemistry, it should be noted that he shared the laurels of the discoverer with two other founders of organometallic chemistry: Edward Frankland (1825–1899), a professor of the Royal Chemical College in London, and August Cahours (1813–1891), a professor of the Ecole Centrale in Paris. It is generally believed that Frankland's first article devoted to the organotin synthesis appeared in 1853⁴⁵. Actually, the results of his pioneer research were published a year earlier in a journal that was of little interest to chemists⁵⁸⁸. There is no reference to this article in monographs and reviews dealing with organotin compounds. Frankland reported in this article that he used his earlier discovered organozinc method for the syntheses of organotin compounds⁵⁸⁸. By the reaction of SnCl_2 with diethylzinc, he first synthesized tetraethylstannane Et_4Sn and studied some of its reactions. In the course of his investigations Frankland⁵⁸⁸ together with Lawrence⁵⁸⁹ first discovered the cleavage reactions of the C–Sn bond.

In the reaction of Et_4Sn with sulfur dioxide in the presence of air oxygen he obtained ethyl triethylstannylsulfonate $\text{Et}_3\text{SnOSO}_2\text{Et}$ ('stantriethylic ethylsulfonate'). The action of H_2SO_4 on the latter led to bis(triethylstannyl) sulfate $(\text{Et}_3\text{SnO})_2\text{SO}_2$ ('stantriethylic sulphate'). Finally, Frankland prepared polydiethylstannylene $(\text{Et}_2\text{Sn})_n$ by the reduction of Et_2SnI_2 with zinc in hydrochloric acid⁴⁵. All these data were reproduced and extended in his later publications^{45,589–591}. In 1853, he isolated crystals of Et_2SnI_2 and some amount of Et_3SnI ⁴⁵ by heating a tin foil with ethyl iodide at 180°C in a sealed tube. He observed this reaction also under sunlight, i.e. he reported the first photochemical process in organometallic chemistry. In 1879, Frankland and Lawrence⁵⁸⁹ demonstrated that the action of R_2Zn ($\text{R} = \text{Me}, \text{Et}$) on Et_2SnI_2 resulted in Et_2SnMe_2 and Et_4Sn , respectively. He found that HCl cleaved Et_2SnMe_2 , but the cleavage products were not identified.

Frankland's^{45,588–591} research is also a corner stone of organotin chemistry. He favored the valence ideas and the use of modern graphic formulas of organotin compounds. Moreover, his research destroyed the border between inorganic and organic chemistry.

In 1852, simultaneously Cahours^{575,583,592–602} together with Löwig and Frankland became interested in organotin compounds. Together with Löwig and Frankland he belongs to the great pioneers of organotin chemistry in the 19th century and he made an essential contribution to its development. His first organotin investigation concerned the synthesis of diethylstannylene (almost simultaneously with those described by Löwig⁴¹ and Frankland⁴⁵) and other reactions followed^{575,592,593}. In 1853, Cahours showed that MeI reacted with Sn at $150\text{--}180^\circ\text{C}$ to give Me_4Sn and Me_3SnI ⁵⁹³. The hydrolysis of Me_3SnI gave $\text{Me}_3\text{SnOSnMe}_3$, whose cleavage with aqueous acids ($\text{HX}, \text{H}_n\text{Y}$) resulted in Me_3SnX

(X = Cl, Br, I, S, OOCMe, NO₃) and (Me₃Sn)_nY (Y = S, CO₃, (OOC)₂, *n* = 2; PO₄, *n* = 3)⁵⁸³. By hydrolysis of Me₂SnI₂, (Me₂SnO)_n was obtained, and it was cleaved with the corresponding acids to Me₂SnX₂^{583,593}. Cahours⁵⁹⁶ was the first to demonstrate the possibility of replacing the halogens in alkylhalostannanes (Et₃SnI, Et₂SnI₂) by the anions of the corresponding silver salts (AgCN, AgNCO, AgSCN) using their reactions with Et₃SnI as an example. He also obtained hexaethyldistannathiane Et₃SnSSnEt₃ by the reaction of Et₃SnCl with H₂S in alcoholic media⁵⁹⁶.

Following these three fathers of organotin chemistry, other luminaries of the chemical science of the 19th century such as Buckton^{603,604}, Ladenburg^{605–607}, and then at the turn of the century Pope and Peachey^{308,608–612} and Pfeiffer and coworkers^{309,613–620}, were engaged in the development of organotin chemistry. In the 20th century this development is associated with the names of well-known scientists such as Krause, Schmidt and Neumann (in Germany), Kraus, Druce, Bullard, Gilman, Rochow, Anderson, Seyferth and West (in the USA), Kocheshkov, Nesmeyanov, Razuvaev, Nefedov, Koton, Kolesnikov and Manulkin (in the USSR), van der Kerk (in the Netherlands), Lesbre (in France) and Nagai and Harada (in Japan) and their numerous colleagues. Together they synthesized about 1800 organotin compounds up to 1960, in *ca.* 950 publications.

We shall now follow systematically these developments.

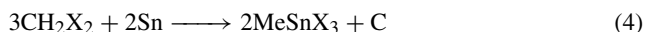
B. Direct Synthesis

The reactions of metals, their intermetal derivatives or alloys (often in the presence of a catalyst or a promoter) with organic halides and with some other organic compounds such as lower alcohols and alkylamines can be regarded as a direct synthesis of the organometallic compounds. As mentioned in Section III.A, Löwig and, to a lesser extent, Frankland were the originators of the direct synthesis of organotin compounds. Since 1860, they were followed by Cahours^{575,583,598,600,602}, who used the reaction of alkyl iodides with a tin–sodium alloy (10–20%) in a sealed tube at 100–200 °C. Cahours⁵⁷⁵ obtained Et₂SnI₂ by the reaction of EtI with tin metal at 140–150 °C as well as at 100 °C under sunlight irradiation (according to Frankland). He also established that by increasing the Na content (from 5 to 20%) in the Sn–Na alloy, the reaction of EtI with the alloys led to the formation of Et₃SnI and then to Et₄Sn. Cahours synthesized a series of trialkylidostannanes R₃SnX^{575,583,598–602} and tetraalkylstannanes R₄Sn (R = Me, Et, Pr)^{575,583,592,598} by the reaction of alkyl iodides with the Sn–Na alloy. Among other products he observed the formation of the corresponding dialkylidiodostannanes and hexaalkyldistannoxanes^{598,600,602}. He found that increasing the sodium content of the alloy led predominantly to tetraalkylstannanes, and decreasing its content led to dialkylidiodostannanes. He also demonstrated that EtBr reacted analogously to alkyl iodides to give Et₃SnBr. Cahours prepared a series of tetraalkylstannanes (C_nH_{2n+1})₄Sn (*n* = 1^{583,594}; 2⁵⁷⁵; 3⁵⁹⁸; 4, 5⁶⁰⁰) by heating the corresponding alkyl iodides and bromides with the Sn–Na alloy in a sealed tube. A simultaneous formation of the corresponding trialkylidostannanes^{575,583,594,598–602} and trialkylbromostannanes⁵⁸³ was observed. Other researchers^{585,589,607,621–625} then synthesized tetraalkyl- and dialkylidihalostannanes by the reaction of alkyl halides with an Sn–Na alloy. Neiman and Shushunov^{626,627} investigated the kinetics of the reaction of tin alloys containing 8.8 and 18.2% Na with EtBr at a wide range of temperatures and pressures in 1948. Depending on the alloy compositions and reaction conditions, the products were Et₄Sn or Et₂SnBr₂. When using this process, they were the first to discover a topochemical reaction with a longer induction period at higher rather than lower temperatures. Following Cahours, they also found that using an alloy with a high Na content led to Et₄Sn. When the sodium content in the alloy

corresponded to a NaSn_4 composition, Et_4Sn was formed at a temperature $<60^\circ\text{C}$, but at $>60\text{--}160^\circ\text{C}$ the main product was Et_2SnBr_2 .

Pure tin was also used for the direct synthesis of organotin compounds. In 1948, unlike previous investigations, Harada obtained sodium stannite Na_2Sn not by the metal fusion, but by the reaction of tin with sodium in liquid ammonia⁶²⁸. The reaction of Na_2Sn with EtBr led to $(\text{Et}_2\text{Sn})_n$.

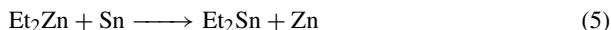
Following Frankland⁴⁵, Cahours^{575,583,598,600,602} established that alkyl halides reacted with melted tin to give dialkyldihalostannanes. Consequently, both authors became the founders of the direct synthesis of organylhalostannanes from metallic tin. Nevertheless, the first attempts to use alkyl bromides in the reaction with tin were unsuccessful^{629,630}. In 1911, Emmert and Eller⁶²² first obtained carbofunctional organotin compounds $(\text{EtCOOCH}_2)_2\text{SnI}_2$ by the reaction of metallic tin with ethyl iodoacetate. In 1928–1929, Kocheshkov^{631–633} discovered that dibromomethane and dichloromethane reacted with tin at $180\text{--}220^\circ\text{C}$ to give almost quantitative yields of MeSnX_3 ($\text{X} = \text{Cl}, \text{Br}$) according to equation 4.



He suggested that $\text{CH}_2=\text{SnX}_2$ was an intermediate product in the process and that MeSnX_3 was formed by addition of HX to the intermediate, which, in turn, was the insertion product of Sn into CH_2X_2 . The reaction of CH_2I_2 with Sn at $170\text{--}180^\circ\text{C}$ led only to carbon and SnI_4 . It is noteworthy that benzyl chloride acted with tin powder in water or in alcohol under mild conditions to give $(\text{PhCH}_2)_3\text{SnCl}$ ⁶³⁴ in 85% yield.

In 1958, Kocheshkov and coworkers⁶³⁵ showed that alkylbromostannane can be prepared from tin and alkyl bromides under ionizing irradiation⁶⁰³.

The development of the direct syntheses of organotins involves a mysterious and even detective story, as told by Letts and Collie^{636–638}. They wanted to prepare diethylzinc according to Frankland by heating ethyl iodide with zinc metal. To their great surprise, tetraethylstannane was the main reaction product⁶³⁶. They could not guess that so much tin was present in the commercial zinc that they purchased. Their further experiments with mixtures of tin and zinc led to the same result. They also found that heating tin powder with EtZnI at 150°C resulted in Et_4Sn ^{636–638}. Consequently, Letts and Collie proposed the following scheme (equations 5 and 6) for the reaction.



Anyway, it is doubtful whether Letts and Collie thought about zinc as the catalyst of the reaction of tin with alkyl halides (in spite of their demonstration) since this fact was established considerably later. The authors also found that the reaction of EtI with a $\text{Sn}\text{--}\text{Zn}$ alloy (33–50%) containing 5% of Cu gave a maximum yield of Et_4Sn . Thus, long before Rochow's finding the catalytic influence of copper in the direct synthesis of organometallic compounds was observed⁶³⁶.

Since 1927, Harada^{639–642} studied the influence of addition of zinc to the $\text{Sn}\text{--}\text{Na}$ alloy in its reaction with haloalkanes (MeI ⁶⁴⁰, EtI ⁶³⁹, PrI ⁶⁴², EtBr ^{641,642} and others). Among other factors, he found that boiling ethyl bromide with an Sn alloy containing 14% of Na and 12–22% of Zn resulted in remarkable Et_4Sn yields. The promotion by zinc during the direct synthesis was further studied by other researchers^{643–648}. In particular, it was shown that Bu_3SnCl ⁶⁴⁹ was the product of the reaction of BuCl and tin–sodium alloy containing 2% of Zn . In 1957, Zietz and coworkers⁶⁴⁹ found that the reaction of higher alkyl chlorides with an $\text{Sn}\text{--}\text{Na}$ alloy containing 2% of Zn at $150\text{--}180^\circ\text{C}$ led to a mixture of R_4Sn and R_3SnCl ($\text{R} = \text{Pr}, \text{Bu}, \text{Am}$) with a high tin conversion. Under milder

conditions, in the same reaction with exactly the same Sn—Na alloy, the product $(R_2Sn)_n$ with $R = Et, Bu$ ⁶⁴⁹, was formed. Cu, Cd, Al⁶⁵⁰ were suggested in 1958 as activators of the alloys of the compositions Na_4Sn (43.5% Na) and Na_2Sn (28% Na). In the presence of these metals, even higher alkyl chlorides (C_8-C_{12}) also reacted with the alloys.

From the end of the 19th century, alkyl chlorides and bromides (often under pressure)^{628,651} successfully reacted with melted tin, preferably in the presence of catalytic amounts of copper or zinc^{652,653}. These data are mostly presented in patents^{643,644,650,654,655}.

In 1953, Smith⁶⁵⁶ patented the reaction of MeCl with Sn, which led to Me_2SnCl_2 at 300 °C. However, already in 1949–1951 Smith and Rochow thoroughly investigated the reaction of gaseous MeCl with melted tin under ordinary pressure, but they did not publish the results though they were presented in a thesis submitted by Smith to Harvard University. The existence of the above patent⁶⁵⁶ induced them to report their result in 1953. Smith and Rochow⁶⁵² studied the influence of added 25 elements to the reaction of methyl chloride with melted tin at 300–350 °C. The best catalysts found were Cu, Ag and Au.

Naturally, copper was further used as a catalyst. Under appropriate conditions, the main reaction product was Me_2SnCl_2 but small quantities of $MeSnCl_3$ and Me_3SnCl were also formed. The yield of Me_3SnCl was increased by the addition of sodium to tin⁶⁵². Methyl bromide reacted with liquid tin at 300–400 °C to form Me_2SnBr_2 ⁶⁵⁷, whereas in these conditions (385 °C) methyl iodide was completely decomposed. The products of the thermolysis were gaseous hydrocarbons and iodine. The iodine reacts with Sn to give SnI_2 and the reaction of SnI_2 with MeI gave $MeSnI_3$ ⁶⁵⁷. In the same article Smith and Rochow⁶⁵⁷ reported that under conditions analogous to those used for the direct synthesis of Me_2SnCl_2 , tin reacted very slowly with EtCl and BuCl underwent a complete thermal decomposition. They also found that MeX ($X = Cl, Br, I$) reacted with tin monoxide containing 10% Cu at 300 °C to form Me_3SnX ⁶⁵⁷.

In 1954, van der Kerk and Luijten⁶⁵⁸ found that in the direct synthesis of tetraorganylstannanes the tin—sodium alloy can be replaced with a tin—magnesium alloy^{659–661}. A mercury catalyst (Hg or $HgCl_2$) was required for this variant and the process was conducted at 160 °C under pressure.

In further investigations it was possible to conduct this reaction at atmospheric pressure in a solvent capable of influencing the ratio of the reaction products R_4Sn and R_3SnX . The method of the alloy preparation played an important role, with the content of magnesium being at most 21–29% (Mg_2Sn). In the absence of the catalyst (mercury salts or amines) alkyl chlorides did not react with these alloys⁶⁵⁰. In the reaction of a Sn—Na alloy (containing 4–5% Cu) with alkyl bromides or iodides in solution, up to 60% of dialkyldihalostannanes R_2SnX_2 as well as R_4Sn and R_3SnX ⁶⁵⁰ were formed.

The direct synthesis of aromatic tin compounds was realized for the first time in the 19th century. In 1889 Polis⁶⁵¹ and in 1926 Chambers and Scherer⁶⁶² obtained tetraphenylstannane by a longtime boiling of bromobenzene with an Sn—Na alloy in the presence of the initiator ethyl acetate⁶⁵¹ or without it⁶⁶². In the reaction of PhBr with an alloy of Li_4Sn composition the yield of Ph_4Sn was only 13%⁶⁶³. Aryl halides did not react with tin alone at temperatures <200 °C⁶⁶⁴. In 1938, Nad' and Kocheshkov⁶⁶⁵ obtained tetraphenylstannane by heating Ph_3SnCl with an Sn—Na alloy. The formation of tetraarylstannanes in the reaction of aryl halides with Sn—Na alloy was probably preceded by arylation of the tin with sodium aryls, which were the intermediates of this process. This mechanism was confirmed by the alkylation of tin with phenylmagnesium bromide⁶⁵⁰. Consequently, organometallic compounds were actually used to synthesize tetraarylstannanes from metallic tin or its alloys with sodium. Thus, in 1938, Talalaeva and Kocheshkov^{666,667} obtained

tetraarylstannanes in a reasonable yield by boiling lithium aryls with tin powder or its amalgam. Nad' and Kocheshkov⁶⁶⁵ carried out the reaction of PhHgCl with an Sn–Na alloy in boiling xylene with better results (50% yield of Ph₄Sn). They found that the reaction between PhHgCl and Na₂Sn involved the intermediate formation of (Ph₂Sn)_n and Ph₃SnSnPh₃. The latter disproportionated to Ph₄Sn and Ph₂Sn. According to their data, the reaction of PhHgCl with Sn gave Ph₂SnCl₂, which was disproportionated to Ph₃SnCl and SnCl₄⁶⁶⁵. The data on the direct synthesis of organotin compounds are summarized in a monograph⁶⁵⁰.

C. Organometallic Synthesis from Inorganic and Organic Tin Halides

Frankland^{588,589,591} was the first to synthesize in 1852 organotin compounds using the reaction of Et₂Zn with SnCl₂ to give Et₄Sn (Section II.A). One year later Cahours⁵⁷⁵ obtained Et₄Sn by the reaction of Et₃SnI with Et₂Zn. He synthesized the first mixed tetraalkylstannane Me₃SnEt⁵⁸³ by the reaction of Me₃SnI with Et₂Zn and in 1862 he analogously prepared Et₃SnMe⁵⁹⁶. Under Butlerov's guidance Morgunov⁶⁶⁸ obtained Me₂SnEt₂ by the reaction of Me₂SnI₂ with Et₂Zn, although they did not succeed in synthesizing it from Et₂SnI₂ and Me₂Zn in the pure form according to Frankland. In 1900, Pope and Peachey⁶⁰⁸ also used the organozinc method to prepare Me₃SnEt. During 12 years they obtained the first organotin compound containing asymmetric tin atom (MeEtPrSnI) using the appropriate dialkyl zinc. The asymmetric iodide was converted into an optically active salt with $[\alpha]_D = +95^\circ$ by the reaction with silver d-camphorsulfonate.

Buckton in 1859 was the first to use tin tetrachloride to synthesize organotin compounds⁶⁰³. At that time, the reaction of SnCl₄ with Et₂Zn was the common route to Et₄Sn. Pope and Peachey⁶⁰⁸ used this method only after four decades. In 1926, Chambers and Scherer⁶⁶² obtained Ph₄Sn by the organozinc method. Kocheshkov, Nesmeyanov and Potrosov⁶⁶⁹ synthesized (4-ClC₆H₄)₄Sn in the same way in 1934. However, at the beginning of the 20th century the organozinc method of organotin compounds synthesis lost its importance.

The use of Grignard reagents led to revolutionary developments in the synthesis of organotin compounds. It started in 1903 when Pope and Peachey⁶¹¹ obtained R₄Sn, R = Et, Ph in a good yield from SnCl₄ and RMgBr. Just one year later this method was used by Pfeiffer and Schnurmann to synthesize Et₄Sn, Ph₄Sn and (PhCH₂)₃SnCl⁶⁷⁰. In 1904, Pfeiffer and Heller⁶¹⁵ reacted SnI₄ with the Grignard reagent MeMgI to obtain Me₃SnI. In 1954, Edgell and Ward⁶⁷¹ used Et₂O and, in 1957, Seyferth⁶⁷² and Stone⁶⁷³ used THF as the solvent in this reaction and that improved the yield of R₄Sn.

From 1914, the Grignard method of synthesis completely displaced the organozinc method and was widely used⁶⁷⁴. Up to 1960, fifty publications reporting the use of this method appeared^{125,675}.

In 1927, Kraus and Callis⁶⁴³ patented the method of preparing tetraorganylstannanes by the reaction of Grignard reagents with tin tetrahalides. In 1926, Law⁶⁷⁶ obtained mixed tetraorganylstannanes, such as Et(PhCH₂)₂SnBu and Et(PhCH₂)SnBu₂ from Et(PhCH₂)₂SnI and Et(PhCH₂)SnI₂, by the Grignard method. In 1923, Böeseken and Rutgers⁶⁷⁷ demonstrated that a Grignard reagent was able to cleave the Sn–Sn bond: the reaction of PhMgBr with (Ph₂Sn)_n led to Ph₄Sn, Ph₃SnSnPh₃ and Ph₁₂Sn₅ (the first linear perorganylpolystannane).

It is noteworthy that in 1912 Smith and Kipping⁶⁷⁸ applied the Barbier synthesis, i.e. the addition of organic halide to a mixture of Mg and SnCl₄ in ether (without preliminary preparation of the Grignard reagent) to obtain organylchlorostannanes in a good yield^{678,679}.

Organolithium synthesis of organotin compounds, in particular $(4\text{-MeC}_6\text{H}_4)_4\text{Sn}$ from SnCl_4 , was first described by Austin⁶⁸⁰ in 1932. In 1942, Talalaeva and Kocheshkov⁶⁶⁷ used this method to obtain Ar_4Sn (e.g. $\text{Ar} = 4\text{-PhC}_6\text{H}_4$) when Grignard reagents failed to react. Bähr and Gelius⁶⁸¹ used the appropriate aryllithiums to synthesize tetra(9-phenanthryl)- and tetra(1-naphthyl)stannane from SnCl_4 . Organolithium compounds were also used to synthesize 1,1-diorganylstannacycloalkanes^{682,683}.

An interesting spirocyclic system was created by the reaction of SnCl_4 with 1,2-bis(2'-lithiumphenyl)ethane by Kuivila and Beumel⁶⁸² in 1958. Spirocyclic compounds were also obtained in the reaction of SnCl_4 with 1,4-dilithium-1,2,3,4-tetraphenylbutadiene^{683,684} or with ethyl bis(2-lithiumphenyl)amine⁶⁸⁵.

In some cases the organolithium compounds cleaved the C—Sn bond^{686–689}. However, these obstacles were successfully overcome by converting the organolithium compounds to the Grignard reagent by adding a magnesium halide^{646,686,688,690}. The organolithium synthesis was also extensively used, especially for attaching vinyl and aryl groups^{686–688,691–702} to the tin atom. It should be noted that in 1955, Gilman and Wu⁶⁹⁴ obtained $4\text{-Ph}_3\text{SnC}_6\text{H}_4\text{NMe}_2$ by the reaction of Ph_3SnCl with $4\text{-Me}_2\text{NC}_6\text{H}_4\text{Li}$. In 1958, Bähr and Gelius⁷⁰³ prepared $(4\text{-PhC}_6\text{H}_4)_3\text{SnBr}$ by reacting $4\text{-PhC}_6\text{H}_4\text{Li}$ with SnBr_4 in a 3.5 : 1 molar ratio.

Both organolithium and organomagnesium syntheses of tetra(*tert*-butyl)stannane had failed⁷⁰⁴. Up to 1960 organolithium compounds were seldom used to synthesize aliphatic tin derivatives⁷⁰⁵. In 1951, the reaction of PhLi with SnCl_2 allowed Wittig and coworkers⁷⁰⁶ to obtain $(\text{Ph}_2\text{Sn})_n$ in a good yield. With excess PhLi , Ph_3SnLi was also formed. Immediately after Wittig's work in 1953, Gilman and Rosenberg⁷⁰⁷ developed a method to synthesize Ar_3SnLi from ArLi and SnCl_2 . The reaction of Ar_3SnLi with appropriate aryl halides gave Ar_4Sn . This method was also successfully used to synthesize tetraalkylstannanes⁷⁰⁸. In 1956, Fischer and Grübert⁷⁰⁹ obtained for the first time dicyclopentadienyltin by the reaction of cyclopentadienyllithium with SnCl_2 .

Ladenburg^{605,606} first used organosodium synthesis (i.e. the Würtz reaction) of organotin compounds in 1871. He synthesized Et_3SnPh by the reaction of Et_3SnI with Na and PhBr in ether medium. That was the first aromatic tin compound. He obtained EtPhSnCl_2 ⁶⁰⁵ in the same way. In 1889, Polis⁶⁵¹ found that the reaction of SnCl_4 with Na and PhCl in boiling toluene did not result in Ph_4Sn . Nevertheless, when a 25% Na —75% Sn alloy reacted with PhBr , using the MeCOOEt as an initiator, he obtained Ph_4Sn . However, during the following century this method was forgotten. Nevertheless, Dennis and coworkers¹⁶⁸ and Lesbre and Roues⁶⁹¹ used the reaction of aryl bromides and Na with SnCl_4 in ether, benzene or toluene to prepare tetraarylstannanes and the method was even patented^{710,711}. Only in 1954–1958 was the Würtz reaction used to synthesize tetraalkylstannanes^{629,712–716}. SnCl_4 could be replaced with alkylchlorostannanes, and Bu_4Sn was obtained in 88% yield⁶²⁹ by the reaction of Bu_2SnCl_2 with BuCl and Na in petroleum ether. Organosodium compounds were used for the synthesis of organotin derivatives in 1954 by Zimmer and Sparmann⁶⁹³, who obtained tetra(1-indenyl)stannane from 1-indenylsodium with SnCl_4 . Five years later Hartmann and coworkers⁷⁰¹ synthesized $(\text{PhC}\equiv\text{C})_4\text{Sn}$ by the reaction of SnCl_4 with $\text{PhC}\equiv\text{CNa}$, and by the reaction of $\text{NaC}\equiv\text{CNa}$ with R_3SnX ($\text{R} = \text{Ar}, \text{PhCH}_2$) they prepared $\text{R}_3\text{SnC}\equiv\text{CSnR}_3$ ^{717,718}.

In 1926, Chambers and Scherer⁶⁶² obtained the first organotin compound containing an Sn—Na bond. By reacting Ph_3SnBr with Na in liquid ammonia, they synthesized Ph_3SnNa and investigated its transformations. For example, the reactions of Ph_3SnNa with aryl halides resulted in Ph_3SnAr , with $\text{ClCH}_2\text{COONa}$, $\text{Ph}_3\text{SnCH}_2\text{COONa}$ was formed, and PhHgI gave Ph_3SnHgPh ⁶⁶². They were the first to cleave the C—Sn bond by metallic Na , demonstrating that Ph_4Sn reacted with Na in liquid ammonia to form consecutively

Ph_3SnNa and Ph_2SnNa_2 . The reaction of the latter with Ph_2SnBr_2 in liquid ammonia gave the polymeric substance $(\text{Ph}_2\text{Sn})_n$ ⁶⁶².

The Würtz-type reaction was applied in the syntheses of organotin compounds, containing an Sn—Sn bond. Law prepared hexabenzylstannane $(\text{PhCH}_2)_3\text{SnSn}(\text{CH}_2\text{Ph})_3$ for the first time in 1926 by the reaction of Na with $(\text{PhCH}_2)_3\text{SnCl}$ in toluene⁶⁷⁶.

Just a few reactions of $\text{R}_{4-n}\text{SnCl}_n$ ($n = 1-4$) with silver^{719,720}, mercury, aluminum, thallium and lead were described^{576,721}. As early as 1878, Aronheim⁷²² found that prolonged heating of Ph_2Hg with SnCl_4 resulted in Ph_2SnCl_2 (33% yield). Only three quarters of a century later PhSnCl_3 ^{723,724} was similarly obtained. In 1930 and 1931, Nesmeyanov and Kocheshkov⁷²⁵⁻⁷²⁷ demonstrated that tin dihalides can react with organomercury compounds. In the reaction of SnX_2 ($\text{X} = \text{Cl}, \text{Br}$) with Ar_2Hg in ethanol or acetone they obtained diaryldihalostannanes Ar_2SnX_2 . In 1922, Goddard and coworkers^{728,729} found that the reaction of SnCl_4 with Ph_4Pb led to Ph_2SnCl_2 and Ph_2PbCl_2 . By the reaction of Ph_3SnCl with $\text{AgC}\equiv\text{CCH}(\text{OEt})_2$, Johnson and Holum⁷³⁰ obtained $\text{Ph}_3\text{SnC}\equiv\text{CCH}(\text{OEt})_2$ in 1958. Finally, in 1957 and 1959, Zakharkin and Okhlobystin^{720,731} found that the reaction of SnCl_4 with R_3Al ^{720,731} could be employed to synthesize tetraalkylstannanes.

In conclusion it should be noted that organometallic synthetic methods of organyl-halostannanes were not as widely used as in the synthesis of the isostructural compounds of silicon and germanium. Section III.E explains the reason for this.

D. Organotin Hydrides

In 1922, Kraus and Greer⁷³² synthesized trimethylstannane Me_3SnH , the first organotin compound containing an Sn—H bond, by the reaction of sodium trimethylstannane with ammonium bromide in liquid ammonia. In 1926, Chambers and Scherer⁶⁶² used this method for the synthesis of triphenylstannane R_3SnH and diphenylstannane R_2SnH_2 . In 1943, Malatesta and Pizzotti⁷³³ obtained Et_3SnH and Ph_3SnH by the same method. In 1951, Wittig and coworkers⁷⁰⁶ used Ph_3SnLi in this reaction. The chemistry of organotin hydrides started to develop extensively when, in 1947, Finholt, Schlesinger and coworkers^{336,648}, who developed the reduction method of organometallic halides by LiAlH_4 , used this method for the synthesis of trimethyl-, dimethyl- and methylstannane from $\text{Me}_{4-n}\text{SnCl}_n$ ($n = 1-3$). This method was widely applied later to obtain organotin hydrides^{48,125,675,734}. Thus, in 1955–1958, Et_3SnI ⁷³⁵, Ph_3SnCl ⁷³⁶, Et_2SnCl_2 ⁷³⁷ and Pr_2SnCl_2 ⁷³⁸ were reduced to the appropriate hydrides by LiAlH_4 . In 1953, West³³⁴ failed to reduce triphenylhalostannanes with zinc in hydrochloric acid, unlike the reduction of triphenylbromogermane. In 1957–1958, Kerk and coworkers^{738,739} developed the reduction method of R_3SnCl to R_3SnH ($\text{R} = \text{Et}, \text{Pr}, \text{Bu}, \text{Ph}$) with amalgamated aluminum in aqueous medium. As a result of this research 20 organotin hydrides $\text{R}_{4-n}\text{SnH}_n$ ($n = 1-3$) became known up to 1960.

Beginning from 1929, Ipatiev and his nearest coworkers Razuvaev and Koton tried to hydrogenate Ph_4Sn under drastic conditions (60 atm, 220 °C)⁷⁴⁰⁻⁷⁴⁴, but neither formation of the compounds containing an Sn—H bond nor hydrogenation of the aromatic cycle was observed. Instead, hydrogenolysis of the C—Sn bond with formation of metallic tin and benzene took place. In this respect we note that, when in 1989 Khudobin and Voronkov⁷⁴⁵ tried to reduce Bu_2SnCl_2 by R_3SiH in the presence of colloidal nickel, the products were metallic tin, butane and R_3SiCl . R_3SiH reduced tetrachlorostannane to SnCl_2 to give R_3SiCl and H_2 . Organotin hydrides $\text{R}_{4-n}\text{SnH}_n$ are not among the stable organotin compounds. Their stability increases (i.e. their reactivity decreases) on decreasing the number n ⁷³⁷ of hydrogens at the tin atom. Even the early researchers observed that many organotin hydrides $\text{R}_{4-n}\text{SnH}_n$ (especially with $\text{R} = \text{Me}$,

Et and $n = 2, 3$) were slowly decomposed at room temperature and easily oxidized by air oxygen^{336,732,735-737,746}. However, Me_3SnH and Me_2SnH_2 are little changed when stored in a sealed ampoule at room temperature during 3 months and 3 weeks, respectively³³⁶. MeSnH_3 decomposed under these conditions less than 2%⁷⁴⁷ during 16 days. Distillation of butylstannane under atmospheric pressure at *ca* 100 °C failed because of its complete decomposition. However, at 170 °C and 0.5 mm the high-boiling triphenylstannane was so stable that its distillation succeeded^{736,738} but it decomposed under sunlight exposure. In 1926, Chambers and Scherer⁶⁶² found that diphenylstannane Ph_2SnH_2 decomposed to Ph_2Sn at $> -33^\circ\text{C}$. In contrast, van der Kerk and coworkers⁷⁴⁸ found that Ph_2SnH_2 decomposed to Ph_4Sn and metallic tin only on heating $>100^\circ\text{C}$ in vacuum. Apparently, this process involves the intermediate formation of $\text{Ph}_2\text{Sn}^{662}$ which further disproportionated. Et_2SnH_2 was decomposed with explosion in contact with oxygen. In 1926-1929 it was shown that oxidation of trialkylstannanes and triphenylstannanes gave different products under different conditions. Bullard and coworkers^{749,750} and later Anderson⁷³⁵ obtained trialkylstannanol. According to Chambers and Scherer⁶⁶², Ph_3SnH gave hexaphenyldistannane. The latter is the product of reaction of Ph_3SnH with amines, as Noltes and van der Kerk⁷⁵¹ had found. Diphenylstannane was dehydrocondensed into the yellow modification of $(\text{Ph}_2\text{Sn})_n$ in the presence of amines. In contrast, the reaction of Ph_3SnH with thiols gave hexaphenyldistannathiane $\text{Ph}_3\text{SnSSnPh}_3$ ⁷⁵¹. In 1950, Indian researchers⁷⁵² found that the reaction of Pr_3SnH with aqueous-alcoholic NaOH solution gave Pr_3SnOH . In 1922, Kraus and Greer⁷³² found that the reaction of Me_3SnH with concentrated HCl led to Me_3SnCl . In 1951, Wittig and coworkers⁷⁰⁶ converted Ph_3SnH to Ph_3SnCl by the same method. Noltes showed in his dissertation (1958) that triorganylstannanes reacted analogously with carboxylic acids to form $\text{R}_3\text{SnOOCR}'$ and that organotin hydrides reacted vigorously with halogens to give the corresponding halides. In 1955, Gilman and coworkers^{267,736} found that Ph_3SnH in the presence of benzoyl peroxide formed Ph_4Sn without precipitation of metallic tin. However, in the presence of excess $(\text{PhCOO})_2$ the product was $\text{Ph}_3\text{SnOCOPh}$. According to Kraus and Greer, and to Chambers and Scherer, R_3SnH ($\text{R} = \text{Me}^{732}$, Ph^{662}) reacted with Na in liquid NH_3 to give R_3SnNa . In 1949, Gilman and Melvin⁷⁵³ pointed out that Ph_4Sn and LiH were formed in the reaction of PhLi on Ph_3SnH . In contrast, Wittig and coworkers⁷⁰⁶ found that the reaction of Ph_3SnH with MeLi led to Ph_3SnLi and CH_4 . Nevertheless, in 1953, Gilman and Rosenberg⁷⁵⁴ found that this reaction resulted in Ph_3SnMe and LiH. Lesbre and Buisson⁷⁵⁵ developed the reaction of trialkylstannanes with diazo compounds ($\text{R}'\text{CHN}_2$), which gave $\text{R}_3\text{SnCH}_2\text{R}'$ ($\text{R} = \text{Pr, Bu}$; $\text{R}' = \text{H, COOEt, COMe, COPh, CN}$) along with nitrogen.

The hydrostannylation reaction⁷⁵⁶ is of great importance in organotin chemistry. This term was proposed by Voronkov and Lukevics^{52,53} in 1964. The reaction is based on the addition of organotin compounds, containing at least one Sn-H bond to multiple bonds ($\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}=\text{O}$ etc.)^{52,53,77,265}. It is of special interest for the synthesis of carbofunctional organotin compounds. This reaction was first carried out by van der Kerk, Noltes and coworkers^{748,751,757,758} in 1956. They found that trialkylstannanes R_3SnH ($\text{R} = \text{Pr, Bu}$) were easily added to the double bonds in $\text{CH}_2=\text{CHR}'$ ($\text{R}' = \text{Ph, CN, COOH, COOMe, CH}_2\text{CN, CH(OEt)}_2$), to give the adducts $\text{R}_3\text{SnCH}_2\text{CH}_2\text{R}'$ in 95% yield. Hydrostannylation proceeded easily in the absence of catalysts by heating mixtures of both reagents at 80-100 °C for several hours. In 1958, monosubstituted ethylene derivatives with $\text{R}' = \text{CONH}_2, \text{CH}_2\text{OH, COCMe, CH}_2\text{OOCMe, 4-C}_5\text{H}_4\text{N, OPh, Hex, C}_6\text{H}_4\text{CH}=\text{CH}_2$ were involved in the reaction with Ph_3SnH . It was found that Ph_3SnH was involved in the hydrostannylation process more easily than trialkylstannanes R_3SnH with $\text{R} = \text{Pr, Bu}^{759}$. For example, the attempted addition of R_3SnH to $\text{CH}_2=\text{CHCH}_2\text{OH}$

had failed, while Ph_3SnH was easily added to allyl alcohol⁷⁵⁶. In 1959, van der Kerk and Noltes⁷⁵⁸ carried out the first hydrostannylation of dienes. The addition of dialkylstannanes to dienes and acetylenes gave polymers in some cases⁷⁵⁹. However, in 1959, Noltes and van der Kerk obtained the cyclic diadduct 1,1,2,4,4,5-hexaphenyl-1,4-distannacyclohexane by the addition of Ph_2SnH_2 to $\text{PhC}\equiv\text{CH}$ ⁷⁵⁸. He also hydrostannylated $\text{Ph}_3\text{GeCH}=\text{CH}_2$ and $\text{Ph}_2\text{Si}(\text{CH}=\text{CH}_2)_2$ with triphenyl- and diphenylstannane. The reaction of Me_3SnH with $\text{HC}\equiv\text{CPh}$ led to $\text{Me}_3\text{SnCH}=\text{CHPh}$ ⁷⁵⁹. Only the *trans*-adduct⁷⁵⁸ was isolated by hydrostannylation of phenylacetylene by triphenylstannane, but its addition to propargyl alcohol gave a mixture of *cis*- and *trans*-adducts. The hydrostannylation of alkynes proceeded more easily than that of alkenes, as confirmed by the lack of reactivity of Ph_3SnH with $\text{HexCH}=\text{CH}_2$, whereas it easily added to $\text{BuC}\equiv\text{CH}$. Nevertheless, in the reaction of R_3SnH with acetylenic hydrocarbons the diadducts^{748,758,759} could also be obtained. Dialkylstannanes R_2SnH_2 ($\text{R} = \text{Pr}^{759}, \text{Bu}^{760}$) were first used as hydrostannylating agents in 1958, and Ph_2SnH_2 in 1959^{758,761}. The addition of R_2SnH_2 to the monosubstituted ethylenes $\text{CH}_2=\text{CHR}'$ at $60-80^\circ\text{C}$ resulted in the diadducts $\text{R}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{R}')_2$ ^{758,760,761} and addition of Ph_2SnH_2 to $\text{F}_2\text{C}=\text{CF}_2$ ^{758,760} at 80°C proceeded similarly. Analogously, organylstannanes RSnH_3 were added to three molecules of unsaturated compounds⁷⁵⁸. Unlike the hydrosilylation reaction, neither Pt nor H_2PtCl_6 catalyzed the hydrostannylation reactions. Addition of hydroquinone did not inhibit this reaction, thus arguing against a free radical mechanism. Dutch researchers^{757,758,760} concluded that the hydrosilylation is an ionic process.

Since 1957 the triorganylstannanes Bu_3SnH and Ph_3SnH attracted scientists' attention as effective reducing reagents. They easily reduced alkyl-⁷⁵⁹, alkynyl-⁷⁵¹ and aryl halides^{748,762}, amines^{748,751} and mercaptans⁷⁵¹ to the corresponding hydrocarbons, but reduced ketones to the corresponding alcohols^{751,763}. Hydrostannylation of the carboxylic group was not observed, distinguishing it from the hydrosilylation. However, Neumann found that in the presence of radical reaction initiators triorganylstannanes were added easily to aldehydes $\text{R}'\text{CH}_2\text{O}$ with the formation of the $\text{R}_3\text{SnOCH}_2\text{R}'$ adducts ($\text{R} = \text{Alk}$; $\text{R}' = \text{Alk}, \text{Ar}$)^{756,764}. Kuivila and Beumel^{765,766} established that the ability of organotin hydrides to reduce aldehydes and ketones was decreased along the series: $\text{Ph}_2\text{SnH}_2 > \text{Bu}_2\text{SnH}_2 > \text{BuSnH}_3 > \text{Ph}_3\text{SnH} > \text{Bu}_3\text{SnH}$. In 1957, Dutch chemists⁷⁴⁸ showed that benzoyl chloride was reduced to benzaldehyde with Ph_3SnH , and Anderson⁷³⁵ discovered that Et_3SnH reduced halides and oxides of Group 13 elements to their lowest oxidation state or even to the free metals. Noltes reported that Pr_3SnH reduced BF_3 and AlCl_3 to the free elements⁷⁵⁶. At the end of the last century, organotin hydrides were widely applied for the reduction of different organic, organometallic and inorganic compounds^{721,767}.

E. Organylhalostannanes. The C—Sn Bond Cleavage

Among the first organotin compounds of special importance are the organylhalostannanes $\text{R}_{4-n}\text{SnX}_n$. We would like to review here their development and approach to their synthesis in the absence of metallic tin, other metals or organometallic compounds, which have not been considered in the previous sections. Their properties will be considered as well.

Historically, the first and basic nonorganometallic method for the synthesis of organylhalostannanes was the C—Sn bond cleavage reaction by halogens and inorganic halides. As reported in section III.A, Frankland⁵⁹¹ and Cahours^{595–597} first observed the C—Sn bond cleavage of tetraalkylstannanes by halogens in 1859 and 1860–1862, respectively. In 1867, following Frankland, Morgunov⁶⁶⁸ demonstrated that the reaction of iodine

with Me_2SnEt_2 resulted in Et_2SnI_2 . In 1871, Ladenburg⁷⁶⁸ found that, depending on the reagent ratio (1 : 1, 1 : 2, 1 : 3), the reaction of Et_4Sn with I_2 resulted in Et_3SnI , Et_2SnI_2 and $\text{IEt}_2\text{SnSnEt}_2\text{I}$, respectively. The cleavage of Et_3SnPh by iodine led to Et_3SnI and PhI ⁶⁰⁶. Thus, he was the first to show that the $\text{Sn}-\text{Ar}$ bond is weaker than the $\text{Sn}-\text{alkyl}$ bond. In 1872, he cleaved Me_4Sn by iodine and obtained Me_3SnI ⁶⁰⁷. Ladenburg⁷⁶⁸ also found that, contrary to Frankland⁵⁹¹, the reaction between iodine and Me_2SnEt_2 led to MeEt_2SnI and Et_2SnI_2 . He demonstrated the $\text{Sn}-\text{Sn}$ bond cleavage by alkyl iodides, e.g. by the reaction of $\text{Et}_3\text{SnSnEt}_3$ with EtI at 220 °C, which gave Et_3SnI and C_4H_{10} ⁷⁶⁸.

In 1900 Pope and Peachey⁶⁰⁸, who intended to synthesize a mixed trialkyl iodostannane having an asymmetric tin atom, cleaved Me_3SnEt and Me_2SnEtPr by iodine and obtained Me_2SnEtI and MeEtPrSnI , respectively. In 1912, Smith and Kipping⁶⁷⁸ demonstrated that it was easier to cleave a PhCH_2-Sn than an $\text{Et}-\text{Sn}$ bond and that cleavage of a $\text{Ph}-\text{Sn}$ was easier in the reaction of $\text{R}_3\text{SnCH}_2\text{Ph}$ ($\text{R} = \text{Ph}, \text{Et}$) with iodine, which led to Et_3SnI and $\text{R}_2(\text{PhCH}_2)_2\text{SnI}$, respectively. Sixteen years later Kipping⁶⁷⁹ found the following decreasing cleavage ability of the $\text{R}-\text{Sn}$ bond: $2-\text{MeC}_6\text{H}_4 > 4-\text{MeC}_6\text{H}_4 > \text{Ph} > \text{PhCH}_2$. He obtained four organotin compounds containing the asymmetric tin atoms: $\text{Ph}(4-\text{MeC}_6\text{H}_4)(\text{PhCH}_2)\text{SnI}$, $\text{Ph}(4-\text{MeC}_6\text{H}_4)(\text{PhCH}_2)\text{SnOH}$, $\text{BuPh}(\text{PhCH}_2)\text{SnI}$ and $\text{EtBu}(\text{PhCH}_2)\text{SnI}$ during the multistage process of the $\text{C}-\text{Sn}$ bond cleavage by iodine followed by a new $\text{C}-\text{Sn}$ bond formation with a Grignard reagent. Unfortunately, he failed to isolate them as pure optically active isomers. In 1924, Krause and Pohland⁷⁶⁹ showed that one of the phenyl groups was cleaved in the reaction of iodine with triphenylhexylstannane. In 1889, Polis⁶⁵¹ found that iodine did not cleave the $\text{Ph}-\text{Sn}$ bond in Ph_4Sn and this was confirmed by Bost and Borgstrom⁷⁷⁰. Steric factors were evidently predominant, i.e. the $\text{Ar}-\text{Sn}$ bond in ArSnR_3 ($\text{R} = \text{Me}, \text{Et}$) was easier to cleave by iodine than the $\text{Sn}-\text{R}$ bond.

Manulkin⁷⁷¹ together with Naumov⁷⁷² extensively studied for the first time the cleavage of alkyl radicals at the tin atom by iodine. They found that their cleavage from R_4Sn ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}, i\text{-Am}$) to form R_3SnI became more difficult (i.e. required higher temperature) on increasing their length. The same was demonstrated for the homologous series of tetraalkylstannanes $(\text{C}_n\text{H}_{2n+1})_4\text{Sn}$ with $n = 1-7$, and for the mixed series $\text{R}_3\text{SnR}'$, where R, R' were alkyl groups of various length^{773,774}. Contrary to Cahours^{595,597}, Manulkin showed that the reaction of iodine with Me_3SnR ($\text{R} = \text{Et}, \text{Bu}, \text{Am}, i\text{-Bu}, i\text{-Am}$) led to Me_2RSnI and that Et_3SnBu was transformed to Et_2BuSnI ⁷⁷⁵. He was also able to cleave two or even all four R groups from the tin atom in R_4Sn ($\text{R} = \text{Me}, \text{Et}$) under more drastic conditions (160–170 °C). Thus, he was the first to find that in the reaction of halogens X_2 with R_4Sn , one or two R substituents were first cleaved in consequent steps whereas the remaining two groups were cleaved simultaneously with the formation of SnX_4 . He was unsuccessful in stopping the process at the RSnX_3 formation. In 1957, Koton and Kiseleva⁷⁷⁶ were the first to demonstrate that the allyl group was easily cleaved from tin atom by iodine: the reaction of iodine with $\text{CH}_2=\text{CHCH}_2\text{SnPh}_3$ led to Ph_3SnI and $\text{CH}_2=\text{CHCH}_2\text{I}$.

Only few publications^{651,777} were devoted to the use of chlorine to obtain organylchlorostannanes. In 1870, Ladenburg⁷⁷⁸ obtained Et_2SnCl_2 by chlorination of hexaethyldistannane $\text{Et}_3\text{SnSnEt}_3$, i.e. a cleavage of both the $\text{C}-\text{Sn}$ and $\text{Sn}-\text{Sn}$ bond took place. In the reaction of hexaethyldistannane with chloroacetic acid at 250 °C he obtained Et_2SnCl_2 as well as C_2H_6 and C_4H_{10} ⁷⁷⁸.

In the 20th century the cleavage reaction of R_4Sn by halogens (mainly by bromine and iodine) was widely used for the syntheses of R_3SnX and R_2SnX_2 , at yields which were dependent on the reaction conditions and the ratios of the reagents. Thus, the first syntheses of organylhalostannanes by the cleavage of R_4Sn and R_3SnX were carried out in

1900–1925^{609,610,630,678,732,769,777,779–782}. Sixty publications in the period before 1960, reporting the use of the cleavage of R_4Sn for organylbromo- and organyliodonstannane syntheses by halogens (mainly bromine and iodine), were reviewed^{125,675}.

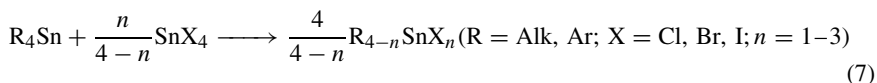
Bromine was mostly used to easily cleave aryl substituents from the tin atom. In 1899 Polis⁶⁵¹ synthesized Ph_2SnBr_2 by the reaction of bromine and Ph_4Sn and in 1918 Krause⁷⁷⁹ obtained Ph_3SnBr by the same reaction. The cleavage of Ph_4Sn by bromine and chlorine to form Ph_3SnX was carried out by Bost and Borgstrom⁷⁷⁰ in 1929. Unlike iodine, ICl reacted extremely easily with Ph_4Sn to give Ph_3SnCl and PhI . In 1931 Bullard and Holden⁷⁸³, and in 1941–1946 Manulkin^{771,773–775} began to investigate in detail the hydrocarbon radical cleavage from the tin atom. The Manulkin studies showed that the tin–alkyl bond became more difficult to cleave as the alkyl group length increased (and it was more difficult when its tail was branched). Secondary alkyl groups (e.g. Me_2CH) were cleaved more easily from the tin atom than primary ones⁷⁷³. These investigations enabled one to arrange the substituents according to the ease of their cleavage by halogens from the tin atom as follows: $All > Ph > PhCH_2 > CH_2=CH > Me > Et > Pr > i-Bu > Bu > i-Am > Am > Hex \geq Heptyl > Octyl$.

Following Frankland⁵⁹¹, Buckton^{604,784} in 1859 demonstrated the possibility of the C–Sn bond cleavage in tetraalkylstannanes by hydrohalic acids. In 1870, Ladenburg⁷⁷⁸ found that HCl cleaved the C–Sn and Sn–Sn bonds in $Et_3SnSnEt_3$ with the formation of Et_3SnCl and that HCl cleaved the phenyl group from $PhSnEt_3$ with the formation of Et_3SnCl ⁶⁰⁵. In 1878, Aronheim⁷²² showed that HCl could cleave two phenyl groups of Ph_2SnCl_2 with the formation of $SnCl_4$. He also reported that the reaction of Ph_2SnCl_2 with the gaseous HBr and HI was not accompanied by the $Ph-Sn$ bond cleavage, but was an exchange reaction, which resulted in Ph_2SnClX ($X = Br, I$). The reaction between Ph_2SnX_2 ($X = Br, I$) and HBr and HI led to SnX_4 .

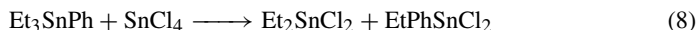
In 1927, Bullard and Robinson⁷⁸⁵ studied the cleavage reaction of Ph_2SnMe_2 by hydrogen chloride, which resulted in Me_2SnCl_2 . Four years later Bullard and Holden⁷⁸³ isolated $MeEtSnCl_2$ from the reaction of HCl with Me_2SnEt_2 . This result showed that both ethyl and methyl groups were cleaved. Under the action of HCl on Et_2SnR_2 , $R = Pr, Ph$ the products $EtPr_2SnCl$ and Et_2SnCl_2 ⁷⁸³ were obtained, respectively. The facility of alkyl group cleavage from the tin atom with hydrogen halides decreased in line with the above-mentioned substituent order with the halogens. However, the order may be different in cleavage by HCl and by iodine. For example, in 1928 Kipping⁶⁷⁹ found that HCl the reaction with $(PhCH_2)_3SnEt$ cleaved the ethyl group, but the reaction of halogens led to the benzyl group cleavage. He also demonstrated that in the reaction of concentrated HCl with tetraarylstannanes two aryl groups might be cleaved⁶⁷⁹. During the action of hydrogen halides on the silicon organotin derivatives $R_2Sn(CH_2SiMe_3)_2$, $R = Me, Bu$ the (trimethylsilyl)methyl group was the first to be cleaved⁶⁷². In contrast, halogens cleaved preferentially the $R-Sn$ bond of these compounds. In 1938, Babashinskaya and Kocheshkov⁶⁹⁶ studied the facility of the reaction of HCl with $Ar_2SnAr'_2$ and found that the C–Sn bond cleavage by hydrogen chloride became more difficult in the following order (the ‘electronegative row’ of substituents): $2-thienyl > 4-MeOC_6H_4 > 1-C_{10}H_7 > Ph > c-C_6H_{11}$. In 1946, Manulkin⁷⁷⁴ showed that $Me_2EtSnCl$ was formed in the reaction of HCl with Me_3SnEt . In 1958, Bähr and Gelius⁷⁰³ cleaved by HCl all the three isomers of $(PhC_6H_4)_4Sn$ to $(PhC_6H_4)_2SnCl_2$. Finally, in 1957, Koton and Kiseleva⁷⁷⁶ demonstrated for the first time that an allyl group easily cleaves from the tin atom under the action of alcoholic HCl solution. The ease of the cleavage followed the order of compounds: $(CH_2=CHCH_2)_4Sn > (CH_2=CHCH_2)_2SnPh_2 > CH_2=CHCH_2SnPh_3$. The cleavage of tetraalkylstannane with HCl at room temperature to $SnCl_4$ was especially easy in this series. Further, the high reactivity in homolytic processes of the C–Sn bond

in the $\text{CH}_2=\text{CHCH}_2\text{Sn}$ moiety was extensively used in synthesis^{786–788}. In 1957–1958, Seyferth^{672,789,790} demonstrated that, under the action of hydrogen halides, a vinyl group was cleaved more easily from the tin atom than an alkyl one, less easily than the phenyl group. In this process an addition of HX to the double bond was not observed. In the 20th century the application of the C–Sn bond cleavage by hydrogen halides was limited. From 1928 to 1948 it was used only in 7 laboratories^{774,783,785,791–794}.

Developed in 1859 by Buckton⁶⁰⁴ and then studied by Cahours⁵⁹⁶ in 1862, by Ladenburg^{605,606} in 1871, by Pope and Peachey³⁰⁸ in 1903 and by Goddard and Goddard⁷²⁹ in 1922, the cleavage reaction of tetraorganylstannane by tin tetrahalides became the most important method for the synthesis of organylhalostannanes. Neumann⁹⁰ named it the co-proportionation reaction (originally '*komproportionierung*'). In general, it may be presented by equation 7.



The first stage of this process is the cleavage of one organic substituent R with the formation of R_3SnX and RSnX_3 . A further reaction of the latter led to R_2SnX_2 and an excess of SnX_4 led to RSnX_3 ⁶⁵³. In 1871, Ladenburg⁶⁰⁶ was the first to show that the presence of both aryl and alkyl groups at the tin atom in the reaction with SnCl_4 led to the reaction described in equation 8.



Unlike the synthesis of organylhalostannanes based on dealkylation by halogens, hydrohalic acids and other inorganic and organic halides of R_4Sn and R_3SnX , the co-proportionation reaction enabled one to keep all the organic substituents in the products, i.e. the number of R–Sn bonds is the same in the precursor and in the products. In 1929–1945, this reaction was studied extensively by Kocheshkov and his coworkers^{633,727,795–806}. In particular, by the reaction of tetraarylstannanes and diarylhalostannanes with SnCl_4 under severe conditions (150–220 °C) they obtained aryltrihalostannanes for the first time. In 1938, Kocheshkov and coworkers synthesized $(4\text{-PhC}_6\text{H}_4)_2\text{SnBr}_2$ by the reaction of $(4\text{-PhC}_6\text{H}_4)_4\text{Sn}$ with SnBr_4 at 160–210 °C. According to Zimmer and Sparmann⁶⁹³ (1954) the reaction of SnBr_4 with Ph_4Sn at 220 °C led to Ph_2SnBr_2 . The reaction of diaryldibromostannanes with SnBr_4 at 150 °C enabled Kocheshkov^{633,795} to obtain a number of aryltribromostannanes in 1929. Two years later he showed that both SnCl_4 and SnBr_4 could be widely used to synthesize ArSnX_3 (X = Cl, Br)⁸⁰⁶. In 1933 he reacted R_4Sn , R_3SnX , R_2SnX_2 (R = Me, Et, Pr) with SnX_4 (X = Cl, Br)⁷⁹⁶. In 1950, Razuvaev⁸⁰⁷ first conducted the photochemical reaction of SnCl_4 with Ph_4Sn and obtained Ph_2SnCl_2 almost quantitatively. This allowed the temperature of the reaction to be reduced to 200 °C^{633,795} and it also showed that the process proceeded via a free-radical mechanism. Unfortunately, these data remained unknown to the general circle of researchers. During the first 60 years of the 20th century the co-proportionation reaction had been referred to in 50 publications^{631,653,798}. In 1957, Rosenberg and Gibbons⁸⁰⁸ used tetravinylstannane in the reaction with SnX_4 at 30 °C which led to $(\text{CH}_2=\text{CH})_2\text{SnCl}_2$.

For the first time tetraiodostannane was used in the reaction with tetraalkylstannanes by Pope and Peachey^{308,611} in 1903. They demonstrated that heating Me_4Sn with SnI_4 at >100 °C led to Me_3SnI and MeSnI_3 . Ph_4Sn did not react with SnI_4 even at 240 °C.

In 1871, Ladenburg⁶⁰⁶ was the first to study the reaction of SnCl_4 with a nonsymmetric tetraorganylstannane. As a result Et_2SnCl_2 and EtPhSnCl_2 were obtained from Et_3SnPh .

In 1945, Pavlovskaya and Kocheshkov⁷⁹⁸ showed that in the reaction of SnCl_4 with triarylalkylstannanes Ar_3SnR , ArSnCl_3 and RSnCl_3 were easily formed. In 1933 Kocheshkov⁷⁹⁶, and in 1963 Neumann and Burkhardt⁸⁰⁹ as well as Seyferth and Cohen⁸¹⁰ found that dialkylidihalostannanes^{662,796,797,800} R_2SnX_2 ($\text{X} = \text{Cl}, \text{Br}$) and alkyltrihalostannanes⁸⁰⁹ reacted with SnCl_4 analogously to tetraalkylstannanes and trialkylhalostannanes, but at a higher temperature (200–215 °C).

In 1878, Aronheim⁷²² was able to disproportionate (i.e. '*retrokomproportionierung*') organylhalostannanes when Ph_2SnCl_2 was transformed to Ph_3SnCl and SnCl_4 , as well as the catalytic influence of NH_3 and sodium amalgam⁸¹¹ on this reaction. He also showed that the reaction of Ph_2SnCl_2 with NaOH led to Ph_3SnCl and SnO_2 , and that the reaction of NaNO_3 with Ph_2SnCl_2 in acetic acid solution resulted in Ph_3SnCl ⁸¹².

During the first half of the 20th century it was found that the C–Sn bond in tetraorganylstannanes could be cleaved by the halides of mercury^{644,703,771,813–815}, aluminum^{816,817}, phosphorus⁶²⁹, arsenic⁸¹⁸, bismuth^{818,819} and iron⁸¹⁷ with formation of the corresponding organylhalostannanes. In this case tetraorganylstannanes acted as alkylating and arylating agents and could be used for preparative purposes.

In 1936 Kocheshkov, Nesmeyanov and Puzyreva⁸²⁰ found that HgCl_2 cleaved the Sn–Sn bond in both R_3SnSnR_3 and $(\text{R}_2\text{Sn})_n$ with the formation of R_3SnCl and R_2SnCl_2 , respectively.

In 1903 and 1904 Pfeiffer and Heller^{309,615} developed a new synthetic approach to organyltrihalostannanes. By conducting the reaction of SnI_2 with MeI in a sealed tube at 160 °C, they obtained MeSnI_3 . In 1911, Pfeiffer⁶¹³ decided to replace in the reaction the SnI_2 by Et_2Sn , which he probably regarded as a monomer. Indeed, heating of $(\text{Et}_2\text{Sn})_n$ with EtI at 150 °C led to Et_3SnI . In 1936, Lesbre and coworkers modified Pfeiffer's reaction⁸²¹. They replaced tin dihalides with the double salts with the halides of heavy alkaline metals MSnX_3 ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$; $\text{X} = \text{Cl}, \text{Br}$), which enabled them to obtain organyltrichloro- and -tribromostannanes. The reaction of KSnCl_3 with excess of RI at 110 °C led to RSnI_3 , $\text{R} = \text{Me}, \text{Et}, \text{Pr}$ with 44, 37 and 25% yields, respectively. In 1953, Smith and Rochow⁸²² found that the reaction of SnCl_2 with MeCl led to MeSnCl_3 .

In 1935, Nesmeyanov, Kocheshkov and Klimova⁸²³ found that the decomposition of the double salts of aryldiazonium chlorides and SnCl_4 , i.e. $[(\text{ArN}_2\text{Cl})_2\text{SnCl}_4]$ (more exactly, $[(\text{ArN}_2)_2]^+[\text{SnCl}_6]^{2-}$), by tin powder gave Ar_2SnCl_2 . Sometimes the reaction product turned out to be ArSnCl_3 . Two years later Waters⁸²⁴ simplified this method by allowing the tin powder to act directly on phenyldiazonium chloride. Later, he found that the reaction proceeded via decomposition of PhN_2Cl into Ph^\bullet and Cl^\bullet radicals, whose interaction with tin led to Ph_2SnCl_2 ⁸²⁵. In 1957–1959 Reutov and coworkers^{826,827} found that the decomposition of double chloronium, bromonium and iodonium salts of tin dichloride $\text{Ar}_2\text{XCl} \cdot \text{SnCl}_2$ by the tin powder led to Ar_2SnCl_2 , ArX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and SnCl_2 . This reaction was simplified by decomposing the mixture of Ar_2XCl and SnCl_2 by the tin powder. In 1959 Nesmeyanov, Reutov and coworkers⁸²⁸ obtained diphenyldichlorostannane by decomposition of complexes of diphenylhalonium dichlorides and SnCl_4 , i.e. $[\text{Ph}_2\text{Y}]_2^{2+}[\text{SnCl}_6]^{2-}$ ($\text{Y} = \text{Cl}, \text{Br}$), by the tin powder.

The attempt of Aronheim⁷²² to obtain PhSnCl_3 by the thermal reaction of SnCl_4 with benzene (analogously to the Michaelis synthesis of PhPCl_2) had failed in 1878. The reaction products at 500 °C were biphenyl, SnCl_2 and HCl . The chemical properties of organylhalostannanes began to be studied extensively after their synthesis. The first property was their ability to be hydrolyzed by water, especially in the presence of bases. As early as 1852–1860 Löwig, Frankland and Cahours obtained $(\text{R}_2\text{SnO})_n$ with $\text{R} = \text{Me}$ ⁵⁸³, Et ^{41,45}; $\text{Et}_3\text{SnSnEt}_3$ ⁵⁸³ and R_3SnOH ($\text{R} = \text{Me}, \text{Et}$)⁵⁸³ by the reaction of alkylhalostannanes with aqueous-alcoholic alkaline solution.

In 1862, Cahours⁵⁹⁶ first showed that the halogen in organylhalostannanes could be easily substituted by a pseudohalide group in the reactions with silver pseudohalides, such as the reaction of Et_3SnI and Et_2SnI_2 with AgCN , AgNCO and AgSCN . In 1878 Aronheim⁷²² substituted the chlorine atom in Ph_2SnCl_2 by the action of HI , H_2O , NH_3 and EtONa which resulted in Ph_2SnClI , $\text{Ph}_2\text{Sn(OH)Cl}$, $\text{Ph}_2\text{Sn(NH}_2\text{)Cl}$ and $\text{Ph}_2\text{Sn(OEt)}_2$, respectively. The products $\text{Ph}_2\text{Sn(OH)Cl}$ and $\text{Ph}_2\text{Sn(NH}_2\text{)Cl}$ were of special interest, since no stable isostructural silicon and germanium analogs had been known. The $\text{Ph}_2\text{Sn(OH)Cl}$ was also obtained by the hydrolysis of $\text{Ph}_2\text{Sn(NH}_2\text{)Cl}$ and it was transformed to Ph_2SnCl_2 by the action of HCl . The stability of $\text{Ph}_2\text{Sn(OH)Cl}$ is amazing, as it does not undergo intramolecular dehydrochlorination. It is more amazing that, according to Aronheim's data, the intermolecular heterofunctional condensation of Ph_3SnCl with Ph_3SnOH resulted in $\text{Ph}_3\text{SnOSnPh}_3$ ⁷²². It might be assumed that compounds $\text{R}_2\text{Sn(X)Cl}$, $\text{X} = \text{OH}$, NH_2 were either dimeric or bimolecular complexes $\text{R}_2\text{SnCl}_2 \cdot \text{R}_2\text{SnX}_2$. In 1879, Aronheim⁸¹² continued to study exchange reactions of Ph_3SnCl . In this respect the interesting investigations of the Russian chemist Gustavson⁸²⁹, who developed the exchange reactions of SnCl_4 with mono-, di- and triiodomethanes, should be mentioned. The mixtures of SnCl_4 with CH_3I , CH_2I_2 and CHI_3 were stored in the dark in sealed ampoules at room temperature for 7 years. No reaction was observed with CHI_3 , but in the mixture of CH_2I_2 with SnCl_4 0.7–1.2% of the chlorine was displaced with iodine, while in the mixture of SnCl_4 with CH_3I 33–34% of the chlorines were displaced. These data should be added to the Guinness Book of Records.

The substitution of alkylhalostannanes by the reaction with silver salts was first realized by Cahours^{592,596}. In 1852 he found that the reaction of Et_2SnI_2 with AgNO_3 and AgSO_4 resulted in $\text{Et}_2\text{Sn(NO}_3)_2$ and Et_2SnSO_4 , respectively⁵⁹². Ten years later he synthesized $\text{Et}_2\text{Sn(SCN)}_2$ and $\text{Et}_2\text{Sn(CN)I}$ in the same way, and Et_3SnCN , Et_3SnSCN and Et_3SnNCO by the reaction of Et_3SnI with AgCN , AgSCN and AgNCO , respectively⁵⁹⁶. In 1860, Kulmiz⁵⁸⁴ used a similar reaction with silver salts for the synthesis of a series of Et_3SnX derivatives (cyanide, carbonate, cyanate, nitrate, phosphate, arsenate, sulfate).

In 1954, Anderson and Vasta⁸³⁰ studied the exchange reactions of Et_3SnX with silver salts AgY . They showed that the substitution ability of X by Y is decreased in the following order of Y ('the Anderson row'): $\text{SMe} > \text{SSnEt}_3 > \text{I} > \text{Br} > \text{CN} > \text{SNC} > \text{Cl} > \text{OSnEt}_3 > \text{NCO} > \text{OCOMe} > \text{F}$. None of these groups could replace the F atom in Et_3SnF . In contrast, the SMe group in Et_3SnSMe can be replaced by any group Y in this series. The simplest synthesis of organylfluoro- and iodostannanes was by the exchange reaction of an appropriate organylchloro- and bromostannanes with alkali metal halides (KF , NaI etc.). The exchange of the halogen atoms of nonfluoro organylhalostannanes for fluorine, i.e. the preparation of organylfluorostannanes, was first realized by Krause and coworkers^{769,781,831–833}, in the reaction of KF and Ph_3SnCl in aqueous-alcohol medium. A number of researchers used the exchange reactions of organylchlorostannanes with the sodium salts of organic and inorganic acids. For example, Kocheshkov and coworkers^{633,795,804} and jointly with Nesmeyanov^{727,806}, and only more than 20 years later Seyferth⁸³⁴, obtained Ar_2SnI_2 by the reaction of Ar_2SnX_2 ($\text{X} = \text{Cl}$, Br) with NaI in acetone or ethanol. In 1929, Kocheshkov^{633,795} found that PhSnCl_3 (which could be easily hydrolyzed by boiling water) reacted with HX ($\text{X} = \text{Br}$, I) in water to give PhSnX_3 .

In the first half of the 20th century it was shown that the C-Sn bond in organotin compounds, especially in tetraorganylstannanes, was easily cleaved by both heterolytic and homolytic mechanisms. This fact makes the C-Sn bond quite different (regarding its thermal and chemical stability) from the C-Si and C-Ge bonds and brought it close to the C-Pb bond. In 1945, Waring and Horton⁸³⁵ studied the kinetics of the thermal decomposition of tetramethylstannane at 440–493 °C, or at 185 °C at a low pressure

(5 mm). Metallic tin, methane and some amounts of ethylene and hydrogen turned out to be the prevalent products of the thermolysis reaction. Indian researchers⁷⁵² revised their data and concluded that the reaction is of a kinetic order of 1.5 and proceeds by a free-radical mechanism. Long⁸³⁶ investigated the mechanism of tetramethylstannane thermolysis in more detail.

In 1958, Prince and Trotman-Dickenson⁸³⁷ studied the thermal decomposition of Me_2SnCl_2 at 555–688 °C in the presence of toluene as the radical carrier. The process proceeded homolytically according to equation 9.



In 1956 and 1959, Dutch researchers^{757,838} first observed the thermal cleavage of $\text{Ph}_3\text{SnCH}_2\text{CH}_2\text{COOH}$, which led to C_6H_6 and $\text{Ph}_2\text{Sn}^+\text{CH}_2\text{CH}_2\text{COO}^-$. The latter was the first zwitterionic organotin compound.

F. Compounds Containing an Sn–O Bond

As reported in Section III.A, oxygen-containing organotin compounds with the stannoxane Sn–O bond, such as $(\text{R}_2\text{SnO})_n$ ^{41,45,583,600,602,722}, $\text{R}_3\text{SnOSnR}_3$ ^{583,598}, R_3SnOH ^{583,598–602} and $[\text{R}(\text{HO})\text{SnO}]_n$ ⁸³⁹, became known in the second half of the 19th century. They appeared first in the laboratories of Löwig (1852), Frankland (1853), Cahours (1860), Aronheim (1878) and Meyer (1883)⁸³⁹. The main synthetic method of compounds of the $(\text{R}_2\text{SnO})_n$ and $\text{R}_3\text{SnOSnR}_3$ type was alkaline hydrolysis of diorganyldihalostannanes and triorganylhalostannanes. In 1913, Smith and Kipping⁷⁸⁰ were the first to report that the so-called diorganyl tin oxides R_2SnO were not monomers, as previously considered. This is the reason why their archaic name has to be taken out of use. They concluded that these compounds were formed in a dehydrocondensation process of the primary hydrolysis products of R_2SnX_2 and were typical polymers, i.e. polydiorganylstannoxane- α,ω -diols $\text{HO}(\text{R}_2\text{SnO})_n\text{H}$, which are solids mostly insoluble in water and organic solvents. The authors succeeded in isolating a low molecular weight oligomeric intermediate, i.e. hexabenzyltristannoxane-1,5-diol $\text{HOR}_2\text{SnOSnR}_2\text{OSnR}_2\text{OH}$ ($\text{R} = \text{PhCH}_2$), from the dehydrocondensation of $\text{R}_2\text{Sn}(\text{OH})_2$. According to Kipping's nomenclature, it was named 'di-unhydro-tri-(dibenzyltin)-dihydroxide'.

In 1951, Solerio⁸⁴⁰ reported that compounds with the R_2SnO formula could be monomeric as well, when the tin atom carries bulky substituents, such as diorganylstannanones $\text{R}_2\text{Sn}=\text{O}$, $\text{R} = \text{C}_{12}\text{H}_{25}$. When the substituents R are less bulky, the substrates are still polymers. Thus, Solerio can be considered as the founder of the chemistry of diorganylstannanones $\text{R}_2\text{Sn}=\text{O}$, the first organotin compounds of three-coordinated tin, bonded to one of its substituents by a double bond.

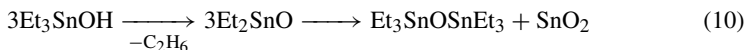
Many years after Löwig's initial study of the oxidation of diethylstannylene to Et_2SnO by air oxygen, the reaction was studied properly in the 20th century by Pfeiffer⁶¹³, Krause and Becker⁷⁸¹ and Chambers and Scherer⁶⁶².

In 1952, Nesmeyanov and Makarova⁸⁴¹ developed the synthetic method for 'diaryltin oxides' Ar_2SnO by the reaction of SnCl_2 with $[\text{ArN}_2]^+[\text{BF}_4]^-$ and with zinc powder in acetone, followed by aqueous hydrolysis with ammonia. The yields of $(\text{Ar}_2\text{SnO})_n$ never exceeded 41%. Along with it small amounts of triarylstannanols and arylstannane acids were isolated. In 1957, Reutov and coworkers⁸²⁶ succeeded in significantly increasing the yields of $(\text{Ar}_2\text{SnO})_n$ up to 80% using the Harada reaction^{628,641,842}. In 1939–1949, Harada^{842,843} described a series of compounds with a composition of $\text{R}_2\text{SnO} \cdot \text{R}_2\text{SnX}_2$ whose molecular structure has not yet been determined.

The Sn–O bond in $(\text{R}_2\text{SnO})_n$ and in $\text{R}_3\text{SnOSnR}_3$ was very reactive. It was hydrolyzed by alkalis, and decomposed by alcohols, glycols⁸⁴⁴ and inorganic and organic acids^{662,722}.

In 1860, Cahours⁵⁸³ began to study nonprotolytic, heterolytic cleavage reactions of the Sn—O—Sn group and showed that polydiethylstannoxane reacted with PCl_5 to give diethyldichlorostannane. The cleavage reactions of this group by SnCl_4 ⁸⁴⁵, SiBr_4 ⁸⁴⁵, HgCl_2 ^{804,846}, I_2 and H_2S ^{631,798,847} were studied only in the 20th century.

During the period 1920–1940, studies of thermal reactions of organotin compounds having Sn—O bonds^{641,662,848–851} had started. All the reactions proceeded with a C—Sn bond cleavage followed by a disproportionation process. In 1926, Chambers and Scherer⁶⁶² found that thermolysis of Ph_3SnOH gave $(\text{Ph}_2\text{SnO})_n$, Ph_4Sn and H_2O . According to Schmitz-DuMont⁸⁵² the product of the dehydrocondensation, i.e. $\text{Ph}_3\text{SnOSnPh}_3$, was also formed. In 1929, Kraus and Bullard⁸⁴⁸ observed an analogous thermal destruction of Me_3SnOH . According to Harada^{641,842,849} (1939–1940) thermolysis of triethylstannanol occurred in another way (equation 10).



Kraus and Bullard⁸⁴⁸ found that $\text{Me}_3\text{SnOSnMe}_3$ thermolysis led to Me_4Sn and $(\text{Me}_2\text{SnO})_n$ ⁸⁴⁸. They also showed that thermal decomposition of $(\text{Me}_2\text{SnO})_n$ gave Me_4Sn , C_2H_6 , SnO_2 and SnO . Unlike this, the thermolysis of $(\text{Et}_2\text{SnO})_n$ led to $\text{Et}_3\text{SnOSnEt}_3$ and SnO_2 ⁶⁴¹. According to Druce^{850,851} (1920–1921) the thermal destruction of $[\text{Me}(\text{OH})\text{SnO}]_n$ resulted in CH_4 , SnO_2 , CO_2 and H_2O . The thermolysis of $[\text{Et}(\text{OH})\text{SnO}]_n$ proceeded in two simultaneous directions to give C_2H_6 , SnO_2 or EtOH and SnO ^{670,851}.

The first trialkylstannanols R_3SnOH , $\text{R} = \text{Me}$, Et were synthesized by Frankland⁴⁵ (in 1853), and Cahours and coworkers^{583,600,602} (in 1860) by the action of alkaline aqueous solutions on the corresponding trialkylhalostannanes. In 1928, Kipping⁶⁷⁹ used aqueous ammonia solution for this purpose. Ladenburg⁶⁰⁶ (1871), Aronheim⁷²² (1878), Hjortdahl⁸⁵³ (1879), Werner and Pfeiffer⁵⁸⁵ (1898) similarly obtained triorganylstannanols. Aronheim⁷²² synthesized triphenylstannanol Ph_3SnOH in 1878. The first trialkylstannanol containing bulky substituents at the Sn atom, $(t\text{-Bu})_3\text{SnOH}$, was synthesized by Krause and Weinberg⁶⁴⁷ in 1930. During the period from 1903 to 1960 trialkylstannanols were mentioned in 50 publications^{675,789,854,855}. In some cases the Sn—OH bond was also formed by hydrolytic cleavage of the $\text{XCH}_2\text{—Sn}$ bond, when X was an electronegative substituent ($\text{N}\equiv\text{C}$, EtOOC).

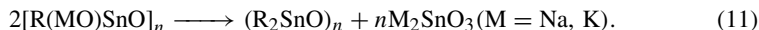
Trialkylstannanols turned out to be rather stable compounds and this was their main difference from their isostructural silicon and germanium compounds^{583,598–602,614,617,647,665,722,856}. They could be dehydrated to hexaalkyldistannoxanes only in the presence of dehydrating agents. For example, Harada⁵⁷⁶ obtained hexamethyldistannoxane from trimethylstannanol only when it was distilled from sodium⁵⁷⁶. Unlike R_3SiOH , the R_3SnOH ($\text{R} = \text{Alk}$) are strong bases^{857,858}. Nevertheless, triphenylstannanol, as well as its silicon analogs are still weak acids⁸⁵⁹. According to the ebullioscopy data, the compounds R_3SnOH ($\text{R} = \text{Me}$, Et , PhCH_2) were associated to some extent^{641,780,848} in boiling benzene. Trialkylstannanols were not converted to stannolates even by the action of Na metal. According to Harada^{639,640} (1927, 1929), the reaction of Me_3SnOH with Na in liquid ammonia did not give Me_3SnNa , but $\text{Me}_3\text{SnSnMe}_3$. Kraus and Neal⁸⁶⁰ also found that the latter was obtained in the reaction of Me_3SnOPh with Na in the same solvent. The reaction of R_3SnOH with inorganic acids (e.g. HCl , HBr , HI , H_2SO_4) enabled an easy replacements of the hydroxyl group by the anions of the acids⁶⁴⁷.

The first attempts to obtain dialkylstannandiols $\text{R}_2\text{Sn}(\text{OH})_2$ by the hydrolysis of dialkylhalostannanes were unsuccessful. These compounds turned out to be extremely unstable and they dehydrated immediately to amorphous polyperorganylstannoxane- α,ω -diols

$\text{HO}(\text{R}_2\text{SnO})_n\text{H}$. However, in the first half of the 20th century diorganylstannandiols containing bulky substituents ($\text{R} = c\text{-Hex}^{769}$, $t\text{-Bu}$, $t\text{-Am}^{647}$) were synthesized.

In 1954, Anderson⁸⁴⁵ concluded that the basicity of organotin compounds having $\text{Sn}-\text{O}$ bonds decreases on increasing the number of oxygen atoms surrounding the Sn atom, i.e. in the series: $(\text{R}_3\text{Sn})_2\text{O} > (\text{R}_2\text{SnO})_n > (\text{R}_2\text{SnO}_{1.5})_n > \text{SnO}_2$.

In the Krause^{647,769} laboratory it was established in 1924 and 1930 that the reaction of $\text{R}_2\text{Sn}(\text{OH})_2$ with HCl or HBr resulted in R_2SnX_2 ($\text{X} = \text{Cl}$, Br). Simultaneously, an interesting disproportionation reaction was discovered according to equation 11.



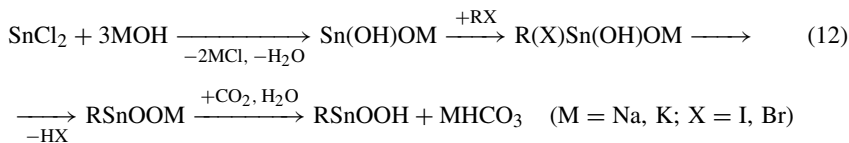
In 1878, first Aronheim⁷²² and then Kipping (1928)⁶⁷⁹ and Krause and Weinberg (1930)⁶⁴⁷ synthesized stable diorganylhalostannanols $\text{R}_2\text{Sn}(\text{OH})\text{X}$, which are stable crystalline substances^{640,650,679}. Organotin compounds $\text{R}(\text{OH})_2\text{SnOSn}(\text{OH})\text{ClR}^{861}$, $\text{RSn}(\text{OH})_2\text{Cl}^{862}$ and $[\text{R}(\text{Cl})\text{Sn}(\text{O})]_n^{862}$ as well as compounds containing the $>\text{Sn}(\text{OH})\text{Cl}$ group were obtained only in the 1960s.

Silicon compounds having the $>\text{Si}(\text{OH})\text{Cl}$ group have not yet been identified. They immediately undergo disproportionation into hydrohalic acid and a short-lived highly reactive diorganylsilanones $\text{R}_2\text{Si}=\text{O}$, which in turn quickly oligomerize or are inserted into the bond of a trapping reagent^{863–866}. The higher stability of diorganylhalostannanols in comparison with their organosilicon analogs can be ascribed to two factors: (1) a longer distance between halogen and oxygen atoms, and (2) a higher stability of the $\text{O}-\text{H}$ bond due to the higher basicity of the $\equiv\text{SnOH}$ group. It is more likely that these compounds are cyclic dimers $[\text{R}_2\text{Sn}(\text{OH})\text{Cl}]_2$ or $[\text{R}_2\text{Sn}(\text{OH})_2 \cdot \text{R}_2\text{SnCl}_2]$, or even high oligomers.

Organylstannantriols $\text{RSn}(\text{OH})_3$ have not yet been isolated. Consequently, organotin compounds $\text{R}_2\text{Sn}(\text{OH})_2$ and $\text{RSn}(\text{OH})_3$ are less stable than their isostructural compounds of silicon and germanium, which in turn are not highly stable. However, their formation as intermediate compounds in hydrolysis reactions of R_2SnX_2 and RSnX_3 seems likely.

The attempted synthesis of organylstannantriols, which was begun by Pope and Peachey³⁰⁸ in 1903 and continued by Kocheshkov and coworkers^{795,801–804,806}, always resulted in obtaining their dehydration products, which were assigned the structure of ‘*organylstannone acids*’ RSnOOH . We use this term although it does not correspond to their structure. In 1883, Meyer⁸³⁹ obtained these compounds, for the first time after developing a simple and efficient method for their preparation, although not in high yields. He found that the action of methyl iodide with aqueous alcoholic solution of sodium stannite (formed from SnCl_2 and NaOH) gives a white crystalline powder which corresponds to the MeSnOOH formula. The latter was easily soluble in hydrochloric acid with the formation of MeSnCl_3 .

Meyer’s reaction can be described by equation 12.



At the same time Meyer also isolated ‘pyro acid’ of $(\text{MeSn})_4\text{O}_7\text{H}_2$ composition. It appeared to be a cross-linked polymer, corresponding to the formula $\text{HO}(\text{MeSnO}_{1.5})_4\text{H}$.

At the beginning of the 20th century Pfeiffer and coworkers^{309,614,615,617,867} and Pope and Peachey³⁰⁸, then Druce^{850,851,868–870} and Lambourne⁸⁷¹ improved the Meyer⁸³⁹ method and synthesized a series of ‘alkylstannone acids’ and studied their

properties. Unfortunately, the Meyer reaction was hardly suitable for the synthesis of arenestannone acids⁸⁷².

In 1903, Pfeiffer and Lehnardt^{309,617} and Pope³⁰⁸, and others^{850,851,868,869,871,873,874} suggested another method for the synthesis of organylstannone acids (as their Na and K salts). It was based on the reaction of alkyltrialostannanes with aqueous alcoholic alkaline solutions. In 1929 following Pope, Kocheshkov and coworkers^{795,801–804} developed a method for the synthesis of arylstannone acids, based on hydrolysis of ArSnCl_3 . It is interesting to note that according to Kocheshkov^{633,795} the hydrolysis of ArSnBr_3 was more difficult than that of ArSnCl_3 . During the hydrolysis of ArSnX_3 by alkali solutions the arylstannates salts were formed, but not the free acids, and then the free acids were isolated by the action of CO_2 . In 1957, Koton and Kiseleva obtained the first unsaturated allylstannone acid by heating tetraallylstannane with water in a sealed ampoule at 170°C ⁷⁷⁶.

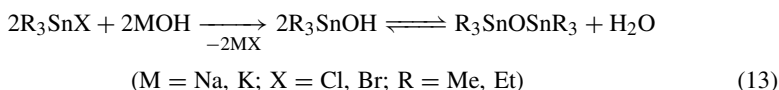
Zhukov⁸⁷⁵ following Pfeiffer and Lehnardt³⁰⁹ and Pope and Peachey (1903)³⁰⁸, Druce^{850,868} and then Kocheshkov and Nad⁷⁹⁹ and Solerio⁸⁷⁶ showed that alkylstannone acids were easily decomposed by hydrohalic acids to RSnX_3 . This reaction was used extensively for the synthesis of pure organyltrialostannanes. In 1938, in Kocheshkov laboratory⁸⁰⁴ it was found that the reaction of RSnOOH with HX proceeded with R-Sn bond cleavage to give RH and SnX_4 under severe conditions. According to Pope and Peachey³⁰⁸, MeSnOOH was transformed in boiling aqueous alkali to a mixture of $(\text{Me}_2\text{SnO})_n$ and Me_3SnOH with simultaneous formation of CH_4 . In 1934, Lesbire and Glotz⁸⁷³ found that the transformation of alkylstannone acids RSnOOH to $(\text{R}_2\text{SnO})_n$ became easier with the decrease in the size of the alkyl radical R . Arenestannone acids did not undergo this reaction.

The so-called organylstannone acids are polymers, which could be assigned the structure of polyorganyl(hydroxy)stannoxanes $[\text{RSn}(\text{OH})\text{O}]_n$ or $\text{HO}[\text{RSn}(\text{OH})\text{O}]_n\text{H}$. It is interesting that they were not hydrolyzed on heating and were not converted to polyorganylstannessesquioxanes $(\text{RSnO}_{1.5})_n$. The properties of their hydrolysis products were strikingly different from those of their isostructural organyltrichlorosilanes with regard to solubility in water and methanol and the high reactivity. They were easily decomposed by acids, alkalis, hydrogen sulfide or mercaptans.

Lambourne^{846,871} showed that the action of carboxylic acids RCOOH on 'methylstannone acid' gave 1,3,5-trimethylpentaacyloxytristannoxanes $\text{Me}(\text{RCOO})_2\text{SnOSn}(\text{OCOR})\text{MeOSn}(\text{OCOR})_2\text{Me}$, which hydrolyzed to the cyclic trimers 1,3,5-trimethyltriacyloxy-cyclotristannoxanes $[\text{Me}(\text{RCOO})\text{SnO}]_3$. The data obtained led him to conclude that methylstannone acid was the cyclic trimer $[\text{Me}(\text{HO})\text{SnO}]_3$.

The first representative of hexaalkyldistannoxanes $\text{R}_3\text{SnOSnR}_3$ with $\text{R} = \text{Et}$ (incorrectly named earlier 'trialkyltin oxides') was obtained by Cahours⁵⁸³ and Kulmiz⁵⁸⁴ in 1860. Unlike their isostructural silicon and germanium analogs, the preparation of lower hexalkyldistannoxanes with $\text{R} = \text{Me}$, Et by hydrolysis of trialkylhalostannanes failed even in the presence of alkalis. This was caused by the fact that the Sn-O-Sn group in these compounds was extremely easily cleaved by water, so that the equilibrium of the trialkylstannanol dehydration with their primary alkaline hydrolysis products (equation 13) was almost completely to the left. Probably, this was the reason that, after the Cahours^{583,598} and Kulmiz⁵⁸⁴ reports, hexaethyldistannoxane appeared in chemical publications again only in 1939^{641,849}. Hexamethyldistannoxane was first synthesized in the Kraus^{782,848} laboratory in 1925–1929 (and then by Bähr⁷⁹⁴), where it was obtained by $\text{Me}_3\text{SnSnMe}_3$ oxidation. In 1940, Harada^{576,842} synthesized $\text{Me}_3\text{SnOSnMe}_3$ by the reaction of Me_3SnOH with metallic sodium. Krause and Pohland⁷⁶⁹ synthesized $\text{Ph}_3\text{SnOSnPh}_3$, the first representative of hexaaryldistannoxanes in 1924. In the last

century, the higher hexaalkyldistannoxanes began to be obtained by dehydration of corresponding trialkylstannanols in the presence of dehydrating agents (P_2O_5 , CaCl_2) or even at high temperature (preferably in vacuum^{642,877–879}). The higher hexaalkyldistannoxanes (beginning from $\text{R} = \text{Bu}$) were synthesized by the reaction of the corresponding trialkylhalostannanes with aqueous⁶⁶² or alcoholic alkaline⁸⁸⁰ solutions. Anderson and Vasta⁸³⁰ obtained $\text{Et}_3\text{SnOSnEt}_3$ by the reaction of Ag_2O with Et_3SnX or with $\text{Et}_3\text{SnSSnEt}_3$.



The properties of hexaalkyldistannoxanes^{583,584,598,641,769,782} were very different in comparison with those of their silicon isostructural analogs $\text{R}_3\text{SiOSiR}_3$. The ability of the $\text{Sn}-\text{O}-\text{Sn}$ group to be decomposed by water, alcohols, phenols, diols^{844,881}, organic and inorganic acids, SH acids (H_2S , RSH)^{584,882}, organic and inorganic halides and pseudohalides is consistent with later investigations, which demonstrated the cleavage of the $\text{Sn}-\text{O}$ bond in $\text{R}_3\text{SnOSnR}_3$, $(\text{R}_2\text{SnO})_n$, $\text{R}_3\text{SnOR}'$ and R_3SnOH by NH acids (RCONH_2 , $(\text{RCO})_2\text{NH}$ ⁷⁵⁹, pyrrole, pyrazole, imidazole, benzotriazole)^{883–885} and by CH acids ($\text{RC}\equiv\text{CH}$ ^{886–893}, $\text{CH}_2(\text{CN})_2$, $\text{CH}_2(\text{COOMe})_2$ ⁸⁹⁴, fluorene), as well as by H_2O_2 ⁸⁹⁵, CO_2 ^{896,897} and RCOCl ⁸⁹⁸. The majority of reactions showed a significant difference between the $\text{Sn}-\text{O}-\text{Sn}$ and $\text{Si}-\text{O}-\text{Si}$ groups. The latter was not decomposed by SH, NH and CH acids, and usually reacted with weak OH acids only in the presence of catalysts.

Anderson⁸⁴⁵ showed that $\text{Et}_3\text{SnOSnEt}_3$ was decomposed by many halides and pseudohalides of B, Si, Ge and Sn, i.e. EtOBCl_2 , $\text{Me}_3\text{SiOCOMe}$, $\text{MeSi}(\text{OCOCF}_3)_3$, $\text{Me}_2\text{Si}(\text{OCOCF}_3)_2$, Ph_2SiF_2 , $\text{MeOSi}(\text{NCO})_3$, SiBr_4 , Pr_3GeF , *i*-PrGeOH, GeCl_4 , SnCl_4 , SnBr_4 , SnCl_2 , Et_2SnCl_2 , PCl_3 , AsCl_3 and SbCl_3 ⁸⁴⁵.

Some classes of compounds having the $\text{Sn}-\text{O}-\text{M}$ moiety (with $\text{M} = \text{C}$, metalloid or metal) can be combined to give a wide range of organotin compounds. The first class, having the $\text{Sn}-\text{O}-\text{C}$ group, include organic compounds of tin with alkoxy, aryloxy or acyloxy groups at the Sn atom. Organylalkoxystannanes $\text{R}_{4-n}\text{Sn}(\text{OR}')_n$, namely Me_3SnOEt , Et_3SnOEt and $\text{Ph}_2\text{Sn}(\text{OEt})_2$, were first obtained by Ladenburg^{899,900} and Aronheim⁷²² in the 1870s. However, the basic investigations of compounds containing the $\text{Sn}-\text{O}-\text{R}$ group were carried out in the 20th century^{41,599,604,653}. They were obtained from the corresponding organylhalostannanes with sodium alcoholates^{860,901–903} or phenolates or by the reaction of organylstannanols, polydialkylstannoxanes, organylacetoxystannanes and organylhalostannanes with alcohols^{881,904} or phenols^{607,714,722,882,900,905,906}. In 1956, Koton⁹⁰⁷ showed the possibility of the $\text{Sn}-\text{C}$ bond cleavage by alcohols. The studied reaction of $(\text{H}_2\text{C}=\text{CHCH}_2)_4\text{Sn}$ led to the cleavage of all four $\text{Sn}-\text{C}$ bonds to give $\text{Sn}(\text{OEt})_4$.

Three years later, D'Ans and Gold⁹⁰¹ found that triorganylaryloxystannanes with electron-withdrawing substituents in the aromatic ring (halogen, NO_2) could be obtained only by the reaction of the corresponding phenols with organylhalostannanes in the presence of sodium hydride in THF. Finally, R. and G. Sasin⁸⁵⁵ succeeded in cleaving the $\text{C}-\text{Sn}$ bond of Et_4Sn by phenol to obtain Et_3SnOPh . Organylalkoxystannanes were interesting synthons due to their high reactivity. Yakubovich and coworkers⁹⁰⁸ first showed the possibility of transforming organylalkoxystannanes to the corresponding organylhalostannanes by reaction with acyl halides in 1958. The reaction of $(\text{Et}_2\text{SnO})_2$ with MeCOF consequently led to $\text{Et}_2\text{Sn}(\text{OEt})\text{F}$ and Et_2SnF_2 together with MeCOOEt .

The first organylacyloxystannanes $R_{4-n}Sn(OCOR')_n$ were obtained by Cahours⁵⁸³ (1860), Kulmiz⁵⁸⁴ (1860) and Frankland and Lawrence⁵⁸⁹ (1879). They were synthesized by the reaction of carboxylic acids or their anhydrides with $(R_2SnO)_n$, R_3SnOH or $R_3SnOSnR_3$. Cahours^{583,598,600} obtained 30 $R_2Sn(OCOR')_2$ and $R_3SnOCOR'$ type compounds with $R = Me, Et, Pr, Bu, i-Bu, i-Am$; $R' = C_nH_{2n+1}$; $n = 0-11$, as well as the corresponding derivatives of hydroxycarboxylic acids (citrates and tartrates) by using this method. Kulmiz⁵⁸⁴ synthesized triethylacyloxystannanes $Et_3SnOCOR'$, $R' = H, Me, Pr, Ph$ and triethylstannyl esters of oxalic and tartaric acids, as well. He also used the reaction of $(Et_3Sn)_2SO_4$ with $Ba(OCOR')_2$ and of $(Et_3Sn)_2CO_3$ with $RCOOH$ for the synthesis of these compounds. Frankland and Lawrence⁵⁸⁹ were less 'pretentious' and had made only triethylacetoxystannane. Further, organylacyloxystannanes were obtained by the Sn—O bond cleavage with carboxylic acids by Quintin⁹⁰⁹ (1930), Kocheshkov and coworkers⁸²⁰ (1936), Smyth⁹¹⁰ (1941), Anderson⁹¹¹ (1957), Shostakovskii and coworkers⁸⁸¹ (1958). By this method the two latter authors obtained trimethylacryloxystannane, which was used further for the synthesis of organotin polymers. Anderson⁹¹¹ synthesized 12 triethylacyloxystannanes by the cleavage of hexaethyldistannoxane with the corresponding halogen-substituted alkanecarboxylic acids.

Another approach to the synthesis of organylacyloxystannanes based on the reaction of organylhalostannanes with salts of carboxylic acids, including silver salts⁸³⁰, was first offered by Pope and Peachey^{608,609} in 1900, then used by Pfeiffer, Lehnard and coworkers⁶¹⁷ in 1910. In 1955–1958 the re-esterification reaction^{905,912} started to be used for the synthesis of organylacyloxystannanes^{905,912}. Anderson^{845,911} (1954, 1957) found that dialkyldiacyloxystannanes were formed in the reaction of $(R_2SnO)_n$ with esters. For the first time the ability of carboxylic acids to cleave the C—Sn bond of R_4Sn was explored by Lesbre and Dupont⁹¹³ (1953), by R. and G. Sasin⁸⁵⁵ and then by Koton and Kiseleva^{776,907} (1957), Seyferth and coworkers^{672,789,790,818} (1957–1958) and Rosenberg and coworkers⁸⁷⁹ (1959).

In the second half of the last century a strong interest was developed in alkylacyloxystannanes due to the discovery of the high fungicide activity of $R_3SnOCOR'$ and the possibility that $R_2Sn(OCOR')_2$ could be applied as polyvinyl chloride stabilizers (see Sections III.J and III.K).

Organylcyanatostannanes $R_{4-n}Sn(OCN)_n$ belong to compounds containing the Sn—O—C group. A series of such compounds with $n = 1$ were synthesized by Zimmer and Lübke⁹¹⁴ (1952) and Anderson and Vasta⁸³⁰ (1954).

Some derivatives of oxygen-containing inorganic acids (such as H_3BO_3 , HNO_3 , H_3PO_4 and H_2SO_4) can be also classified as belonging to organotin compounds, having the Sn—O—M group, where M is a metalloid. Unlike the isostructural organosilicon compounds, trialkylstannyl and dialkylstannyl derivatives of strong inorganic acids have an ionic structure, so they can be referred to as organotin salts. As early as 1898 Werner and Pfeiffer⁵⁸⁵ showed that diethylstannylenesulfate Et_2SnSO_4 (which has no monomeric organosilicon analog) and many other similar compounds were dissociated in water into Et_2Sn^{2+} and SO_4^{2-} ions. In the 19th century the first organotin salts of this kind were obtained by Löwig⁴¹: Et_2SnSO_4 , $Et_2Sn(NO_3)_2$, Et_3SnNO_3 , $(Et_3Sn)_2SO_4$; by Cahours^{583,599}: Me_2SnSO_4 , $(Me_3Sn)_2SO_4$, $(Et_3Sn)_2SO_4$, Et_2SnSO_4 , $(i-Bu_3Sn)_2SO_4$, $Et_2Sn(NO_3)_2$; by Buckton⁶⁰⁴: $(Et_3Sn)_2SO_4$; by Kulmiz⁵⁸⁴: $(Et_3Sn)_2CO_3$, Et_3SnNO_3 , $(Et_3Sn)_2SO_4$, $(Et_3Sn)_3PO_4$, $(Et_3Sn)_3AsO_4$; by Frankland⁵⁸⁹: $(Et_3Sn)_2SO_4$; and by Hjortdahl^{621,853}: $(Me_3Sn)_2SO_4$, $(Et_3Sn)_2SO_4$, $(Et_3Sn)_2SeO_4$. In 1898 Werner and Pfeiffer⁵⁸⁵ obtained Et_2SnHPO_4 and Et_2SnSO_4 . Six years later Pfeiffer and Schnurmann⁶⁷⁰ described $(Et_3Sn)_2CO_3$ again.

After these investigations, organotin salts did not attract attention until almost the middle of the 20th century. In the second half of the 20th century interest in these compounds increased sharply owing to the discovery of some useful properties of organotin compounds having the Sn—O—M group. During these years numerous organotin salts with $M = B^{915,916}$, N^{917} , $P^{790,918-921}$, As^{922} , $S^{623,673,782,905,923}$, Se and $I^{915,924}$ were synthesized (only the periodical publications are cited here). A large number of patents cited in a review⁶³¹ were devoted to these salts.

Na and Li stanolates belong to these compounds, since they have Sn—O—M groups ($M = \text{metal}$). Unlike the isostructural compounds of silicon and germanium, the preparation of R_3SnOM ($M = Na, Li$) by the direct reaction of sodium and lithium with the appropriate stannanols had failed. Compounds of these type were synthesized by Chambers and Scherer⁶⁶² in 1926, and later by Harada⁶⁴¹ via the oxidation of R_3SnNa in 1939. In 1963 Schmidbaur and Hussek⁹²⁵ obtained R_3SnOLi by the cleavage of hexaorganyl-distannoxanes with organolithium compounds. Me_3SnOLi turned out to be a hexamer. The attempt of Harrison⁹²⁶ to obtain Bu_3SnOLi by cleavage of $(Bu_2SnO)_n$ with butyllithium resulted in the formation of Bu_4Sn .

Dimethylstannylenes salts of inorganic acids, which came to light in Rochow's laboratory in 1952–1953^{915,924}, could be assigned to organotin compounds, having the Sn—O—M group with $M = Sb, V, Mo, W$. They were obtained by the reaction of Me_2SnCl_2 with the corresponding acids and their salts in the aqueous medium. Rochow attributed the ease of such reactions to the complete dissociation of Me_2SnCl_2 in water to the Me_2Sn^{2+} and Cl^- ions.

In 1959, Wittenberg and Gilman⁹²⁷ obtained dimethylstannylenes salts of phosphorus, arsenic, molybdenic and tungsten acids by the reaction of Me_2SnCl_2 with the corresponding acids. In 1950–1960, many compounds containing the Sn—O—Si group were synthesized by the reaction of triorganylsilanates of alkaline metals with organylhalostannanes^{928–936}. In 1952, $Ph_3SnOSiPh_3$ and $(Me_3SiO)_2Sn^{937}$ were synthesized by the reaction of Ph_3SiONa and Me_3SiONa with Ph_3SnBr and $SnCl_2$, respectively. In 1957, Papetti and Post⁹²⁸ obtained $Ph_3SnOSiPh_3$ by reacting Ph_3SiONa with Ph_3SnCl . In 1961, Okawara and Sugita⁹³⁸ synthesized triethyl(trimethylsilyloxy)stannane $Et_3SnOSiMe_3$ and found that its reaction with CO_2 gave $(Et_3Sn)_2CO_3$. Okawara and coworkers^{939–941} (1950, 1961) obtained tetraalkyl-1,3-bis(trimethylsilyloxy)distannoxanes $R_2(Me_3SiO)SnOSn(OSiMe_3)_2R_2$ ($R = Me, Et, Pr, Bu$), which turned out to be dimeric, by co-hydrolysis of R_2SnCl_2 with Me_3SiCl in aqueous ammonia. These compounds were recently shown to be centrosymmetric tricyclic ladder dimers in which all the tin atoms were pentacoordinated⁹⁴². The syntheses of these compounds by co-hydrolysis of Me_3SiCl with $ClR_2SnOSnR_2Cl$ were carried out in order to confirm their structures. Labile dialkylbis(trimethylsilyloxy)stannanes $R_2Sn(OSiMe_3)_2$ were obtained similarly. All these compounds tended to disproportionate to form α, ω -bis(trimethylsilyloxy)polydialkylstannoxanes. These investigations founded the basis for the chemistry of stannosiloxanes^{640,910,926,943,944} and their practical use.

In the middle of the 20th century synthetic methods started to develop, and the properties⁹²⁶ were studied of metal–stannoxane monomers and polymers having a Sn—O—M group, where $M = Ge, Pb, Ti, P$, as well as their analogs, containing SnEM ($E = S, Se, Te, NR$) chains.

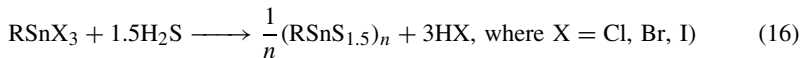
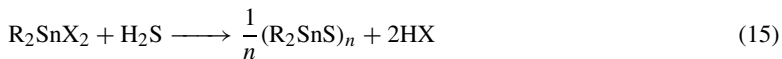
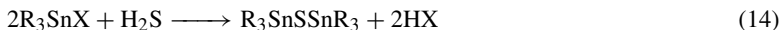
G. Compounds Containing an Sn—E Bond ($E = S, Se, N, P$)

Unlike silicon and germanium, tin and lead belong to the family of chalcophile elements (according to the Goldschmidt geochemical classification), which have a high affinity to sulfur. In this connection the stability of the stannathiane Sn—S bond (in the Sn—S—Sn

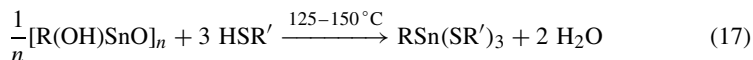
group) and the ease of its formation differ strongly from the high reactivity of the Si—S and the Ge—S bonds. The Sn—S bond can be compared with the siloxane bond in the Si—O—Si group. Consequently, the distannathiane Sn—S—Sn group has a special place in organotin chemistry^{88,125,675,757,945} just like the disiloxane Si—O—Si group, which played a most important role in organosilicon chemistry.

The first reaction, which showed the easy conversion of the Sn—O to the Sn—S bond, is due to Kulmiz^{584,946}. In 1860, he found that triethylstannanol could be converted to hexaethyldistannathiane $\text{Et}_3\text{SnSSnEt}_3$ by reaction with hydrogen sulfide. In 1953, Sasin showed that hydrogen sulfide easily cleaved the distannoxane group in hexaalkyldistannoxanes⁸⁸² with the formation of hexaalkyldistannathianes. Analogously, trialkylalkoxystannanes⁸⁸ reacted with H_2S . Hydrogen sulfide also cleaved the Sn—O bonds in the oligomers $(\text{R}_2\text{SnO})_n$ and polymers $[\text{R}(\text{OH})\text{SnO}]_n$. After Kulmiz's investigations, organotin compounds containing the Sn—S bond did not attract the attention of chemists until the end of the 19th century, probably because of their low reactivity and the reluctance to work with hydrogen sulfide and its derivatives. However, in the first half of the last century the incredible ease of the Sn—S bond formation was supported again by the easy cleavage of the Sn—O bond and other Sn—X bonds ($\text{X} = \text{halogen, H, Sn}$ and even $\text{C}^{789,818}$) by H_2S . In 1903, Pfeiffer and Lehnardt^{309,614} found that the action of H_2S on methyltrihalostannanes gave an unknown polymethylstannanesquithiane $(\text{MeSnS}_{1.5})_n$, which was assigned the $(\text{MeSn}=\text{S})_2\text{S}$ structure. Analogously, in 1931, Nesmeyanov and Kocheshkov^{727,806} obtained the first polyarylstannanesquithianes $(\text{ArSnS}_{1.5})_n$ by the reaction of H_2S with aryltrihalostannanes.

Pfeiffer and coworkers⁶¹⁶ (1910), and then Kocheshkov^{796,947} and Nesmeyanov^{727,806,815} (1931–1933) carried out the easy hydrothiolysis of organotin halides $\text{R}_{4-n}\text{SnX}_n$, $n = 1-3$ (equations 14–16).



With organosilicon halides, the same reactions proceeded only in the presence of an acceptor of hydrogen halide. In the first half of the last century the monomeric structures were assigned to $\text{R}_2\text{Sn}=\text{S}$ and $(\text{RSn}=\text{S})_2\text{S}$, obtained in the reactions mentioned above. In 1942, Harada^{948,949} and later other investigators^{924,950,951} found that the compounds of the composition R_2SnS ($\text{R} = \text{Ph}$) were cyclic trimers $(\text{Ph}_2\text{SnS})_3$, i.e. hexaphenylcyclotristannathianes. It is remarkable that the reactions of organylhalostannanes with alkali metals or ammonium sulfides and hydrosulfides as well as with H_2S proceed smoothly even in aqueous medium^{727,815}. This method for the synthesis of $(\text{Ar}_2\text{SnS})_3$ was first proposed by Kocheshkov⁸⁰² and Nesmeyanov and Kocheshov^{727,806} in 1931 and used later by them^{801,804,952} and by Harada^{642,948,949}, Seyferth⁶⁷² and Edgar and Teer⁹⁵³ for the syntheses of compounds of the $\text{R}_3\text{SnSSnR}_3$ and $(\text{R}_2\text{SnS})_3$ ⁸⁰⁴ series. In 1938, first Nad' and Kocheshkov⁶⁶⁵ and then Pang and Becker⁹⁵⁴ obtained hexaaryl distannathianes. The first representatives of the hexaalkyldistannathiane series $\text{R}_3\text{SnSSnR}_3$, $\text{R} = \text{Me, Et, Pr}$ were obtained by Harada^{948,949} in 1942. Organyl(organylthio)stannanes $\text{R}_{4-n}\text{Sn}(\text{SR}')_n$ containing the Sn—S—C group were first obtained in the 1950s. It was found that the Sn—O bonds in the Sn—O—Sn and Sn—OH groups were easily cleaved by mercaptans like hydrogen sulfide. That was evidently proved by the reaction studied by Stefl and Best⁹⁵⁵ (1957) and Ramsden and coworkers⁹⁵⁶ (1954) (equation 17).



Cycloalkyldistannoxanes (R_2SnO)₂ were also cleaved by thiols $\text{R}'\text{SH}$ to give $\text{R}_2\text{Sn}(\text{SR}')_2$ ^{956,957}. As is evident by the numerous patent data, not only alkane- and alkenethiols, but also their carbofunctional derivatives such as mercaptoalcohols, mercaptoacids and their ethers and esters, were applied in the reaction with organotin compounds containing an Sn—O bond. Pang and Becker⁹⁵⁴ obtained the first triorganyl(organylthio)stannane Ph_3SnSPh in 1948. In 1953–1958, Sasin and coworkers^{882,958} synthesized a series of trialkyl(organylthio)stannanes $\text{R}_3\text{SnSR}'$ ($\text{R} = \text{Et, Pr}$; $\text{R}' = \text{Alk, Bn, Ar}$). In 1957–1961, compounds of this series⁹⁵⁹, including Ph_3SnSPh ⁹⁶⁰, were obtained by the reaction of sodium thiolates with organotin halides. The first patents dealing with the methods of obtaining organyl(organylthio)stannanes by the reaction of the corresponding halides and mercaptans in the presence of an HHal acceptor were issued in 1953–1956^{961–963}.

Whereas aliphatic and aromatic thiols cleaved the C—Sn bond in tetraalkylstannanes to give trialkylorganylthiostannanes^{768,855}, the analogous reaction in organosilicon chemistry is absolutely unusual. According to Seyferth^{789,818} (1957), the vinyl group was especially easy to cleave from tin atom by mercaptans.

In 1933, Bost and Baker⁹⁶⁴ first carried out the C—Sn bond cleavage by elemental sulfur. They recommended the reaction of Ar_4Sn and S as a method for the synthesis of Ar_3SnSAr . Furthermore, in 1962–1963 Schmidt, Bersin and Schumann^{965,966} (for a review, see Reference⁹⁶⁷) studied the cleavage of Bu_4Sn , Ph_4Sn and Ph_3SnCl by sulfur. In spite of the high stability of the Sn—S—Sn group in comparison with the Sn—O—Sn group, in 1954 Anderson⁸⁴⁵ was able to cleave it by the action of $n\text{-C}_{12}\text{H}_{25}\text{SiI}_3$, SiBr_4 , GeCl_4 , SnCl_4 , SnCl_2 , PCl_3 and AsCl_3 on $\text{Et}_3\text{SnSSnEt}_3$ with the formation of Et_3SnX ($\text{X} = \text{Cl, Br, I}$) together with the corresponding inorganic sulfides.

In 1950, Tchakirian and Berillard⁸⁷⁴ obtained for the first time organotin compounds containing the Sn—Se bond. Those were polyalkylstannasesquiselenanes $(\text{RSnSe}_{1.5})_n$ which were formed by the reaction of $[\text{R}(\text{OH})\text{SnO}]_n$ with H_2Se . Monomeric compounds containing the Sn—Se bonds were synthesized in the 1960s. The cleavage reactions of the Sn—O bonds by H_2Se were unprecedented.

The majority of organotin compounds containing the stannazane Sn—N bond appeared only in the early 1960s. Their late appearance was probably caused by the fact that the reaction of organylhalostannanes with ammonia, primary and secondary amines did not result in the corresponding amino derivatives (as for the isostructural Si and Ge derivatives), but in stable complexes containing a hypervalent tin atom (Section III.I). The first compound containing the Sn—N bond, triethylstannylisocyanide Et_3SnNC , was synthesized by Kulmiz⁵⁸⁴ by the reaction of Et_3SnI with AgCN in 1860. He also obtained *N*-triethylstannylcarbamide and this synthesis was no longer reproduced. In 1927, Bullard and Robinson⁷⁸⁵ obtained a mixture of $(\text{Me}_3\text{Sn})_3\text{N}$ and Me_3SnPh by the reaction of Me_3SnNa with PhBr in liquid NH_3 , but they failed to isolate tris(trimethylstannyl)amine. Nevertheless, they can be considered as the founders of modern synthetic methods of organotin compounds having Sn—N bonds. In 1930, Kraus and Neal⁹⁶⁸ reported success in obtaining amino(trimethyl)stannane Me_3SnNH_2 by the reaction of hexamethyldistannane or trimethylstannane with sodium amide in liquid ammonia. However, they could neither isolate it nor describe its properties. Between 1930 and 1960 only organotin sulfonamide derivatives^{88,714,969–971}, trialkylstannylisocyanates R_3SnNCO ⁸³⁰ and isocyanides R_3SnNC ^{714,795,830,924,972} were synthesized, but many organotin complexes containing the $\text{N} \rightarrow \text{Sn}$ bonds were obtained (Section III.I). Kettle⁹⁷³ (1959) pointed out the formation of

aminodimethylstannylsodium $\text{Me}_2\text{Sn}(\text{NH}_2)\text{Na}$ by the reaction of dimethylstannane with sodium in liquid ammonia. Up to 1960 no compound of the type $\text{R}_{4-n}\text{Sn}(\text{NR}^1\text{R}^2)_n$ had been synthesized.

A revolutionary breakthrough, which marks the birth of the most important compounds containing the Sn–N bond, was made by Wiberg and Rieger⁹⁷⁴. They patented the preparation method of trialkyl(alkylamino)stannanes by the reaction of trialkylchlorostannanes with lithium alkylamides. In 1962, this method was improved by Abel and coworkers⁹⁷⁵ and Jones and Lappert⁹⁷⁶ and was further widely practiced. Jones and Lappert⁹⁷⁶ synthesized 23 compounds by this method and studied their numerous addition and insertion reactions. In the same period Sisido and Kozima developed a method for obtaining trialkyl(dialkylamino)stannanes based on the reaction of trialkylchlorostannane with dialkylaminomagnesium bromides⁹⁷⁷. In 1962, Abel and coworkers⁹⁷⁵ also developed an original exchange method to synthesize trialkyl(alkylamino)stannanes by Si–N bond cleavage using trialkylbromostannanes according to equation 18.



The intermediate of this process was a complex of the precursor reagents, which decomposed to the final reaction products.

This pioneer research marked the start of vigorous development of the chemistry of organotin compounds containing Sn–N bonds^{862,973}. Numerous publications appeared in reviews^{737,738,926,949,973,978,979} as well as in parts 18 and 19 of Gmelin's Handbook⁸⁷.

The first compound containing the Sn–P bond was synthesized in 1947 by B. Arbuzov and Pudovik⁹⁸⁰, who applied the A. Arbuzov reaction to organotin halides by demonstrating that R_3SnX reacted with $\text{P}(\text{OR}')_3$ at 105 °C with the formation of $\text{R}_3\text{SnPO}(\text{OR}')_2$ ($\text{R} = \text{R}' = \text{Me}, \text{Et}$). The Sn–P bond in these compounds was easily cleaved by Cl_2 , HCl , MeCOCl and aqueous KOH . The reaction of Et_3SnI with $\text{NaPO}(\text{OEt})_2$ in EtOH gave $\text{Et}_3\text{SnSnEt}_3$. In 1947 Arbuzov and Grechkin showed that R_2SnX_2 reacted with $\text{P}(\text{OMe})_3$ with the formation of $\text{R}_2\text{Sn}[\text{PO}(\text{OMe})_2]_2$ ⁹¹⁸. The reaction of MeSnI_3 and $\text{P}(\text{OMe})_3$ resulted in $\text{MeSn}[\text{PO}(\text{OMe})_2]_3$. The reaction of Et_2SnI_2 with $\text{NaPO}(\text{OEt})_2$ proceeded in two directions with the formation of $\text{Et}_2\text{Sn}[\text{PO}(\text{OEt})_2]_2$ and Et_2Sn . The latter was oxidized to Et_2SnO ⁹⁸⁰ by the air oxygen. In 1959, Kuchen and Buchwald⁹⁸¹ obtained R_3SnPPh_2 by the reaction of R_3SnBr with Ph_2PNa .

Organotin compounds having Sn–As and Sn–Sb bonds were mentioned briefly in a patent⁹⁸² issued in 1935.

Since 1963, a number of organotin compounds in which the tin atom was bonded to B, P, As and Sb atoms were synthesized. However, these studies are beyond the period of history covered in this chapter.

H. Compounds Containing Sn–Sn or Sn–M Bond

Compounds containing the Sn–Sn bonds corresponding in general to the R_3SnSnR_3 and $(\text{R}_2\text{Sn})_n^*$ formulas appeared in the early days of organotin chemistry. Until the middle of the 20th century, these compounds were considered as the three-valent (R_3Sn) and two-valent (R_2Sn) tin derivatives³³⁴.

As described in Section III.A, the first compound of this type was polydiethylstannane $(\text{Et}_2\text{Sn})_n$, which was synthesized by Löwig⁴¹ in 1852 as one of the products of the reaction

* Hereafter, oligomers and polymers $(\text{R}_2\text{Sn})_n$ will be denoted as R_2Sn unless otherwise noted, and monomers, i.e. (diorganylstannylenes), as R_2Sn .

of ethyl iodide and a tin–sodium alloy, and by Frankland in 1853 by reducing Et_2SnI_2 with zinc in the HCl^{45} . In 1859–1860, Buckton⁶⁰⁴ and Cahours⁵⁷⁵ synthesized the same compound. Already in 1911, Pfeiffer⁶¹³ obtained R_2Sn , $\text{R} = \text{Me}$, Et by reducing R_2SnCl_2 with sodium amalgam in ether. In 1925, Kraus and Greer⁹⁸³ synthesized Me_2Sn by the reaction of Me_2SnBr_2 and Na in liquid ammonia. Excess of Na gave Me_2SnNa_2 ^{641,983}. Harada^{628,641} used this method to obtain Et_2Sn . In 1925, Kraus and Greer⁹⁸³ synthesized Me_2Sn by the reaction of Me_2SnNa_2 and Me_2SnBr_2 . In 1959, Kettle⁹⁷³ synthesized Me_2Sn by the reaction of metallic sodium and Me_2SnH_2 followed by decomposition of Me_2SnNa_2 obtained by ammonium bromide.

In 1920, Krause and Becker⁷⁸¹ for the first time prepared Ph_2Sn by the reaction of SnCl_2 and PhMgBr . In 1923, Böeseken and Rutgers⁶⁷⁷ observed the formation of Ph_2Sn when Ph_2SnNa_2 reacted with Ph_2SnBr_2 in liquid ammonia. In 1926, Chambers and Scherer⁶⁶² reacted Ph_2SnBr_2 and Na in liquid ammonia to synthesize Ph_2Sn .

In 1939–1959 $\text{Me}_2\text{Sn}^{973,983}$, $\text{Et}_2\text{Sn}^{628,641,649,842}$, $\text{Ph}_2\text{Sn}^{706,984-986}$ and their analogs were obtained by the methods described above.

It should be mentioned that the compounds of structure R_2Sn , which were once considered as monomers and later proved to be oligomers or polymers $(\text{R}_2\text{Sn})_n$, did not always correspond to this formula. In 1964, Neumann and König⁹⁸⁷ pointed out that when Ph_2Sn was synthesized by the reaction of alkali metals and Ph_2SnX_2 , not only a Sn–Sn bond but also C–Sn bonds were created, making the structure of the formed polymers more complicated. The latter polymers were assigned the $\text{R}_3\text{Sn}(\text{R}_2\text{Sn})\text{SnR}_3$ and $\text{R}(\text{R}_3\text{Sn})_2\text{Sn}(\text{R}_2\text{Sn})_n\text{SnR}_3$ ($\text{R} = \text{Ph}$)^{806,987,988} structures. However, at the same time the cyclic oligomer dodecaphenylcyclohexastannane $(\text{Ph}_2\text{Sn})_6$ was isolated in the reaction of SnCl_2 and PhMgBr together with the higher oligomers and polymers⁹⁸⁷. In 1961, Kuivila and coworkers⁹⁸⁹ showed that Ph_2SnH_2 in the presence of amines underwent the dehydrocondensation to perphenylcyclostannanes $(\text{Ph}_2\text{Sn})_n$. Neumann and König⁹⁸⁷ obtained a series of dodecaphenylcyclohexastannanes in a high yield from the corresponding Ar_2SnH_2 in the presence of pyridine. In the dehydrocondensation of Ph_2SnH_2 in DMF they succeeded in obtaining $(\text{Ph}_2\text{Sn})_5$. Consequently, four-, five-, six- and nine-membered peralkyl-, perbenzyl- and percyclohexylcyclostannanes $(\text{R}_2\text{Sn})_n$ ^{988,990,991} with $\text{R} = t\text{-Bu}$, PhCH_2 ($n = 4$); $c\text{-Hex}$ ($n = 5$); Et , Bu , $i\text{-Bu}$ ($n = 6, 9$) were synthesized using this method. Thus, the investigations of Neumann and König^{987,990,991} clarified the structures of the compounds corresponding to the $(\text{R}_2\text{Sn})_n$ composition.

The first representative of hexaorganyldistannanes R_3SnSnR_3 with $\text{R} = \text{Et}$ was obtained in 1860 by Cahours⁵⁷⁵ and then in 1869–1872 by Ladenburg^{607,768,900,992}. Cahours isolated $\text{Et}_3\text{SnSnEt}_3$ from the reaction products of EtI with a tin–sodium alloy and Ladenburg synthesized it from the reaction of Et_3SnI and metallic Na. Ladenburg determined the molecular weight of the product of Et_3SnI with Na by its vapor elasticity. This enabled him to assign the $\text{Et}_3\text{SnSnEt}_3$ formula to the product, instead of Et_3Sn , as was considered before and even some time later. In 1908, Rügheimer⁹⁹³ repeated this synthesis and carried out a precise measurement of the molecular weight (MW) of $\text{Et}_3\text{SnSnEt}_3$ in ether by the ebullioscopic method. He found that the MM value decreased on dilution. When the solvent to substance ratio was 5.55 : 1, the MW was 235, and when it was 38.7 : 1, MW = 368 (for Et_6Sn_2 , MM = 411). These data apparently indicated that hexaethyl-distannane was dissociated to the free radicals $\text{Et}_3\text{Sn}^{\bullet}$ ⁹⁹³ in the dilute solutions. Rügheimer followed Ladenburg by pointing out that this compound was the derivative of four-valent tin and contained an Sn–Sn bond. In 1917, Grüttner⁹⁹⁴ (the same method was used later by Kraus and Eatough⁹⁹⁵) obtained R_3SnSnR_3 ($\text{R} = \text{Et}$, Pr , $i\text{-Bu}$) from R_3SnCl and Na at 120 °C by a similar method and corroborated Ladenburg's data when he determined the molecular mass of hexaethyl-distannane by cryoscopy in benzene. He also

synthesized the mixed hexaalkyldistannanes of $\text{REt}_2\text{SnSnEt}_2\text{R}$ ($\text{R} = \text{Pr}$, *i*-Bu)⁹⁹⁴ from REt_2SnBr and Na.

Only in 1925 did Kraus and Bullard⁹⁹⁶ and Kraus and Session⁷⁸² obtain hexamethyldistannane by the reaction of Me_3SnBr with Na solution in liquid ammonia. In 1929, Harada⁶⁴⁰ described the preparation of $\text{Me}_3\text{SnSnMe}_3$ by the reaction of Me_3SnOH and sodium in liquid ammonia. In 1924, Krause and Poland⁷⁶⁹ obtained hexacyclohexyldistannane by the reaction of SnCl_4 and *c*-HexMgBr. In 1926, Law synthesized $(\text{PhCH}_2)_3\text{SnSn}(\text{CH}_2\text{Ph})_3$ by the reaction of Na with $(\text{PhCH}_2)_3\text{SnCl}$ ⁶⁷⁶. In 1937, Riccoboni⁹⁹⁷ developed a synthesis of R_3SnSnR_3 by the electrochemical reduction of R_3SnCl in methanol.

Krause and Becker⁷⁸¹ in 1920 synthesized the first representative hexaaryldistannane $\text{Ar}_3\text{SnSnAr}_3$ ($\text{Ar} = \text{Ph}$) by the reaction of triaryl bromostannane and sodium in liquid ammonia. Krause and Weinberg⁸³² synthesized a series of other hexaaryldistannanes in 1929. According to Nad' and Kocheshkov⁶⁶⁵ hexaaryldistannanes were among the reaction products of arylmercurochlorides and tin-sodium alloy. In 1920, Krause and Becker⁷⁸¹ (and later Bonner and coworkers⁹⁹⁸) established that when the reaction of SnCl_4 with PhMgBr was carried out under defined conditions, it lead to $\text{Ph}_3\text{SnSnPh}_3$. Hexaaryldistannane with $\text{R} = 2\text{-PhC}_6\text{H}_4$ ⁹⁹⁹ was obtained analogously.

The attempt of Kraus and coworkers^{782,1000,1001} to obtain compounds $(\text{R}_3\text{Sn})_4\text{C}$ by the reaction of CCl_4 and R_3SnNa ($\text{R} = \text{Me}$, Et, Ph) gave instead R_3SnSnR_3 . In 1951, Razuvaev and Fedotova⁹⁸⁵ found that R_3SnSnR_3 could be prepared by the reaction of $(\text{R}_2\text{Sn})_n$ and $\text{Ph}_3\text{CN}=\text{NPh}$. Wittig and his coworkers⁷⁰⁶ (1951) and Gilman and Rosenberg^{767,1002} (1952) offered a convenient method for the synthesis of $\text{Ph}_3\text{SnSnPh}_3$ by the reaction of Ph_3SnLi with Ph_3SnX ($\text{X} = \text{Cl}$, Br). In 1953, Gilman and Rosenberg⁷⁰⁷ also found that the main reaction product of $(2\text{-MeC}_6\text{H}_4)_3\text{SnLi}$ with 2-iodotoluene was R_3SnSnR_3 ($\text{R} = 2\text{-MeC}_6\text{H}_4$).

In contrast, in the reaction of Ph_3SnLi with EtI or PhCH_2Cl they obtained Ph_4Sn and Ph_3SnR ⁷⁶⁷ ($\text{R} = \text{Et}$, CH_2Ph). The interaction of Ph_3SnNa with O_2 , CO_2 , SO_2 , PhCOCl and PhSSPh ⁹⁶⁰ gave $\text{Ph}_3\text{SnSnPh}_3$.

Finally, $\text{Ph}_3\text{SnSnPh}_3$ was formed slowly in the reaction of Ph_3SnM ($\text{M} = \text{Li}$, Na) with Et_2O , THF, EtOH and BuOH. Wittig and coworkers⁷⁰⁶ showed that the action of lithium on Ph_3SnBr in liquid ammonia followed by treatment with NH_4Br led to a mixture of $\text{Ph}_3\text{SnSnPh}_3$ and Ph_3SnH . As reported in Section III.D, hexaphenyldistannane was formed by the dehydrocondensation of Ph_3SnH in the presence of aliphatic amines⁷⁵¹. $\text{Ph}_3\text{SnSnPh}_3$ was also formed on reduction of carbonyl compounds by triphenylstannane. It is remarkable that according to Johnson and coworkers^{1003,1004} 1,2-dihalotetraalkyldistannanes were formed in the reaction of R_2SnCl_2 with EtONa or with highly basic amines in ethanol. Finally, it must be remembered that dodecaorganylpentastannanes $\text{R}(\text{R}_2\text{Sn})_n\text{SnR}_3$ containing 5 tin atoms ($n = 4$) in a linear chain were first synthesized by Böeseken and Rutgers⁶⁷⁷ in 1923 (with $\text{R} = \text{Ph}$) and by Kraus and Greer⁹⁸³ in 1925 (with $\text{R} = \text{Me}$). The latter authors also described $\text{EtMe}_2\text{SnMe}_2\text{SnMe}_2\text{Et}$, which is unstable in air. In 1932, Kraus and Neal⁸⁶⁰ obtained dodecamethyltetraastannane ($\text{R} = \text{Me}$, $n = 3$). Individual linear peroorganylpolyastannanes containing more than five Sn atoms in the chain were unknown until 1956¹⁰⁰⁵. Böeseken and Rutgers⁶⁷⁷ synthesized the first bulky perorganyloligostannane, i.e. tetrakis(triphenylstanny)stannane $(\text{Ph}_3\text{Sn})_4\text{Sn}$, by the reaction of Ph_3SnNa and SnCl_4 . One cannot but mention that macrocyclic perethylcyclostannanes $(\text{Et}_2\text{Sn})_n$ with $n = 8$, 9¹⁰⁰⁶, 10¹⁰⁰⁷ were synthesized in 1963. Thus, the possibility that ten tin atoms can be bonded to each other in a closed chain was shown.

Peroorganylstannylmetals $R_3SnMR'_3$ ($M = Si, Ge$) were first obtained in the laboratory of Kraus^{161,782,996} by the reaction of R_3SnX with R'_3MNa (formed by the action of Na on R'_3MX). In 1933, Kraus and Eatough⁹⁹⁵ obtained $Ph_3SnSiMe_3$ by the reaction of Ph_3SnLi with Me_3SiCl . Afterward, Gilman and Rosenberg⁷⁶⁷ synthesized $Ph_3SnSiPh_3$ by the reaction of Ph_3SnLi with Ph_3SiCl in 1952. In 1961, Blake and coworkers⁹⁶⁰ obtained $Bu_3SnSiMe_3$ ⁹⁶⁰ by the reaction of Bu_3SnLi and Me_3SiCl . Analogously, Gilman and Gerow²¹⁷ synthesized $Ph_3SnGePh_3$ by the reaction of Ph_3SnCl with Ph_3GeK in 1957. The attempt of Buckton⁶⁰⁴ to obtain a compound containing a Sn—Pb bond failed in 1859, but three quarters of a century later the synthesis of $Me_3SnPbPh_3$ was patented⁹⁸². In all the studies mentioned above it was demonstrated that the Sn—Sn bond is more reactive than the Si—Si and the Ge—Ge bonds and is closer in reactivity to the Pb—Pb bond.

Chemical transformations of organotin compounds containing the Sn—Sn bond started to develop in the 19th century by Cahours⁵⁷⁵ (1860) and Ladenburg⁹⁰⁰ (1870). They found that halogens cleaved this bond easily in $(R_2Sn)_n$ and R_3SnSnR_3 to form R_2SnX_2 and R_3SnX , respectively. In the last century the reaction of halogens with R_2Sn and R_3SnSnR_3 was carried out in the laboratories of Krause^{647,769,781,831} (1918–1929), Böeseken⁶⁷⁷ (1923), Kraus^{161,782,995} (1925, 1927, 1933), Law⁶⁷⁶ (1926), Kocheshkov⁶⁶⁵ (1938) and Gilman²¹⁷ (1957).

Kraus and Session⁷⁸² (1925), Kraus and Bullard⁹⁹⁶ (1926), Harada⁶⁴¹ (1939) and Brown and Fowbes¹⁰⁰⁸ (1958) observed that R_3SnSnR_3 is slowly oxidized by the air oxygen to $R_3SnOSnR_3$.

In 1925, Kraus and Session⁷⁸² showed that elementary sulfur reacted easily with the Sn—Sn bond of hexaalkyldistannanes to form hexaalkyldistannathianes.

In 1908, Rügheimer⁹⁹³ observed that hexaalkyldistannane were slowly oxidized by air to $R_3SnOSnR_3$ under exposure to air. In 1870, Ladenburg⁷⁷⁸ showed that $Et_3SnSnEt_3$ was cleaved by H_2SO_4 with the formation of inflammable gas and an oil-like product, which crystallized on cooling and was probably Et_2SnSO_4 . When the latter was recrystallized from the hot HCl, Et_2SnCl_2 was isolated. Ladenburg obtained Et_3SnCl and Sn by the reaction of $Et_3SnSnEt_3$ with $SnCl_4$. Therefore, he was the first to discover that hexaalkyldistannanes possess reductive properties. In 1871, Ladenburg was also the first to cleave the Sn—Sn bond by organic halides. The reaction of $Et_3SnSnEt_3$ with EtI at $220^\circ C$ led to Et_3SnI and butane, but with $ClCH_2COOH$ it led to Et_2SnCl_2 , C_2H_6 , C_4H_{10} and CO_2 ⁷⁶⁸. Continuing this research, Ladenburg⁶⁰⁶ cleaved $Et_3SnSnEt_3$ by MeI (at $220^\circ C$) and $ClCH_2COOEt$. In 1917, Grüttner⁹⁹⁴ followed these studies and showed that hexaalkyldistannanes were cleaved by EtI at $180^\circ C$ to R_3SnI and $EtSnR_3$ ($R = Et, Pr, i-Bu$). He also reported that hexaalkyldistannanes were slowly oxidized by air to $R_3SnOSnR_3$. Krause and Pohland⁷⁶⁹ and Kraus and Bullard⁹⁹⁶ found an unusual reaction of hexamethyldistannane with $CaCl_2$ in the presence of air, which led to trimethylchlorostannane. In 1917, Grüttner⁹⁹⁴ first showed that hexaethyldistannane was cleaved by $HgCl_2$ to give Et_3SnCl and mercury. Then Kraus and Session⁷⁸² (1925) and Kocheshkov, Nesmeyanov and Puzyreva¹⁰⁰⁹ (1937) carried out an analogous reaction. In 1936, the latter authors⁸²⁰ found that the Sn—Sn bond in hexaethyldistannane was cleaved by aromatic organomercury compounds Ar_2Hg and $ArHgCl$, with the formation of Et_3SnAr and metallic mercury (with $ArHgCl$, Et_3SnCl was also formed). The products Et_2SnAr_2 and Hg were obtained in the reaction of Ar_2Hg with Et_2Sn . The reactions of $HgCl_2$ with $Et_3SnSnEt_3$ and Et_2Sn gave Hg as well as Et_3SnCl and Et_2SnCl_2 , respectively.

During 1917–1957 it was found that the Sn—Sn bond was also cleaved by $AgNO_3$ ^{641,781,831}, $BiBr_3$ ⁹⁹⁴, sodium amide⁹⁶⁸ and organolithium compounds^{217,707}.

The ability of the Sn—Sn bond to be cleaved by alkali metals was first established by Kraus and Session⁷⁸² in 1925. They found that hexaorganylstannanes were cleaved by sodium in liquid ammonia to give triorganylstannylsodium^{148,227,782}. Subsequently, Gilman and Marrs²⁴⁶ showed that lithium could also cleave hexaphenyldistannane in THF. The Sn—Sn bond in R_2Sn was as reactive as that in R_3SnR_3 and was similarly cleaved by the reagents mentioned above. For example, in 1911 Pfeiffer and coworkers⁶¹⁸ reported that reactions of Et_2Sn with oxygen and halogens resulted in the formation of Et_2SnO and Et_2SnX_2 ($X = Cl, Br, I$), respectively. In 1958, Bähr and Gelius discovered an unusual reaction of R_2Sn ($R = 2-, 3-$ and $4-PhC_6H_4$) with $SnCl_2$, which led to Sn and R_3SnSnR_3 ⁹⁹⁹. The latter product with $R = 2-PhC_6H_4$ was isolated in two crystal modifications. The precursor $(2-PhC_6H_4)_2Sn$ was the cyclic trimer, since its molecular weight determined in 1,2-dibromoethane after careful purification is 1300¹⁰¹⁰.

I. Compounds of Nontetracoordinated Tin

Already in 1862 Cahours⁵⁹⁶ obtained adducts with the composition $R_3SnI \cdot 2B$ ($R = Me, Et; B = NH_3, i-C_5H_{11}NH_2, PhNH_2$) and for the first time he drew attention to the tendency of organotin compounds to complex with organic bases and ammonia. One quarter of a century later, Werner and Pfeiffer⁵⁸⁵ reproduced these data and obtained complexes $Et_3SnI \cdot 2B$. They also obtained complexes with the composition $Et_2SnX_2 \cdot 2B$ ($X = Cl, Br, I; B = NH_3, Py$) and considered their structure according to Werner's coordination theory¹⁰¹¹. Richardson and Adams¹⁰¹² reported adducts with the composition $SnX_4 \cdot 4[PhNH_2 \cdot HX]$ ($X = Cl, Br$). Werner assigned to the latter complex the $[SnX_2(HX \cdot PhNH_2)_4]X_2$ structure, and the Richardson complexes were probably mixtures of $[PhNH_3]_2^+[SnX_6]^{2-}$ and $2PhNH_2 \cdot HX$. Twenty-seven years later Pfeiffer and coworkers^{309,618,620} continued the research of his teacher. He obtained and studied many complexes of organotin halides with amines which contained a hexacoordinated Sn atom, namely $Me_2SnI_2 \cdot 2Py$ (1903)³⁰⁹; $R_2SnX_2 \cdot 2Py$ ($R = Me, Et, Pr, Bu, Ph, 4-MeC_6H_4; X = Cl, Br, I$); $MeSnX_3 \cdot 2Py$ ($X = Cl, Br$) (1911)⁶¹⁸; $R_2SnX_2 \cdot 2B$ ($R = Me, Et, Pr; X = Cl, Br, I; B = PhNH_2, Py, quinoline$) (1924)⁶²⁰. At that time he and then others described the adducts $Pr_{4-n}SnX_n \cdot 2B$ ($B = Py; n = 1-3$) containing hexacoordinated tin atom^{616-618,1013-1015}. In 1911 he obtained the $RSnX_3 \cdot 2Py$ ⁶¹⁸ complexes. Pfeiffer and coworkers^{309,618} also synthesized the first complexes of the type $R_{4-n}SnX_n \cdot 2B \cdot 2HX$ ($R = Me, Et, Pr, Ph; X = Cl, Br; B = Py, quinoline, PhNHMe, PhNH_2; n = 1-3$). It may be assumed that the structure of these complexes corresponded to the $[BH^+]_2[R_{4-n}SnX_{n+2}]^{2-}$ formula with a hexacoordinated Sn atom. Ten years later Druce^{850,851,868,1016} obtained the similar adducts $RSnX_3 \cdot 2B \cdot 2HX$. It can now be stated that these complexes corresponded to the general formula $[BH]_2^+[RSnCl_5]^{2-}$ ($R = Me, Et, i-Pr; B = Py, PhNH_2, PhMeNH$), as well as to $\{[PyH]_2^+[i-PrSnBr_5]^{2-}\}$ ^{851,868,1016}.

In 1923, Kraus and Greer⁷⁷⁷ obtained the 1 : 2 complexes of Me_3SnX ($X = Cl, I$) and Me_2SnCl_2 with $NH_3, PhNH_2$ and pyridine. Within a year Krause and Pohland⁷⁶⁹ obtained the adduct $(c-C_6H_{11})_3SnCl \cdot NH_3$, which was prepared despite the presence of three bulky substituents at the tin atom. In 1937, Karantassis and Basillides⁶²⁴ described a series of complexes of the composition $Me_2SnI_2 \cdot 2B$ ($B = Py, PhNH_2, 2-MeC_6H_4NH_2, PhNEt_2, 4-MePy, 2-methylquinoline$). In 1934, Kocheshkov¹⁰¹⁴ obtained the adducts of $R_{4-n}SnX_n \cdot 2Py$ ($R = Me, Et; X = Cl, Br$) and, in 1936, the $Et_3SnBr \cdot NH_3$ adduct⁸²⁰. One such complex, namely $(Me_2SnCl_2 \cdot 2Py)$, was obtained in the Rochow laboratory in 1957¹⁰¹⁵. In 1934–1935, Kocheshkov and coworkers^{799,803,1014} prepared the complexes of Py and aryltrialostannanes $ArSnX_3 \cdot 2Py$. In 1958, Reutov and coworkers¹⁰¹⁷

synthesized a series of coordinated compounds of the composition $[\text{ArN}_2]_2^+[\text{MeSnCl}_5]^{2-}$ and $[\text{ArN}_2]_2^+[\text{Et}_2\text{SnCl}_4]^{2-}$. In 1959, Nesmeyanov, Reutov and coworkers⁸²⁸ obtained the unusual complexes $[\text{Ph}_2\text{I}^+]_2[\text{SnCl}_4\text{Y}_2]^{2-}$, containing hexacoordinated tin atom, by the reaction of diphenylhaloiodides Ph_2IY with SnCl_4 . Reaction of these complexes with tin powder gave Ph_2SnCl_2 .

Almost all these complexes had a hexacoordinated tin atom in octahedral environment. It is remarkable that only five intermolecular coordination compounds $\text{Me}_3\text{SnX} \cdot \text{B}$ (Cl , Br , I ; $\text{B} = \text{NH}_3^{777,782,1001,1018}$, Py^{777} , PhNH_2^{777}) containing pentacoordinated tin atom were obtained in 1923–1934. In 1901, Kehrman¹⁰¹⁹ described an unusual 1 : 1 complex of triphenylchloromethane with tetrachlorostannane. The formula $[\text{Ph}_3\text{C}]^+[\text{SnCl}_5]^-$ could describe its structure. Unlike it and according to Gustavson⁸²⁹, methyl iodide (as well as H_2Cl_2 and HCl_3) did not form the addition products in the reaction with SnCl_4 , but the reactants were involved in a very slow exchange reaction between the iodine and chlorine atoms. The tin atom in the 1 : 1 complexes is placed in the center of a trigonal bipyramid^{1020–1022} or have the ionic tetrahedral structure $[\text{Me}_3\text{SnB}]^+\text{X}^-$. The simple statistics mentioned above indicate that the complexes of the pentacoordinated tin atom were less stable thermodynamically, and consequently they were easily converted into their analogs having the hexacoordinated Sn atom.

In 1924, Pfeiffer and coworkers⁶²⁰ reported the existence of the sole adduct $\text{Et}_2\text{SnCl}_2 \cdot 3\text{NH}_3$, in which the tin atom was heptacoordinated. In the fourteen years 1910–1924, Pfeiffer had shown that intermolecular complexes, having octacoordinated tin atom, are not rarities. He obtained $\text{Ph}_2\text{SnBr}_2 \cdot 4\text{Py}^{616}$, $\text{MeSnI}_3 \cdot 4\text{Py}^{618}$, $\text{Ph}_2\text{SnCl}_2 \cdot 4\text{Py}^{618}$, $\text{Me}_2\text{SnI}_2 \cdot 4\text{NH}_3$, $\text{Et}_2\text{SnCl}_2 \cdot 4\text{NH}_3$ and $\text{Et}_2\text{SnBr}_2 \cdot 4\text{NH}_3^{620}$. It could not be stated unequivocally that the tin atom in these complexes was octacoordinated. However, it is probable that their structure corresponded to the formula $[\text{R}_4-n\text{SnB}_4]^{n+}\text{X}^-$ in which the Sn atom was hexacoordinated and the complexes are salts or ion pairs. As a whole, according to Gol'dshtein and coworkers^{1023,1024} the tendency of organylchlorostannanes for complexing decreased in the following series: $\text{PhSnCl}_3 > \text{Bu}_2\text{SnCl}_2 > \text{Ph}_2\text{SnCl}_2 > \text{Ph}_3\text{SnCl} > \text{Bu}_3\text{SnCl}$, i.e. with the decreasing number of chlorine atoms at the central Sn atom.

Alkylhalostannanes form stable complexes with oxygen-containing ligands. First, the aliphatic organotin bases having an Sn–O bond in which the oxygen atom has a strong nucleophilic reactivity belong to such ligands. The first complex of such a type, $\text{Et}_2\text{SnO} \cdot \text{Et}_2\text{SnI}_2$, was obtained by Strecher¹⁰²⁵ in 1858. From 1914¹⁰²⁶ complexes of the compositions $(\text{R}_2\text{SnO})_n \cdot \text{R}_2\text{SnX}_2^{641,1026,1027}$ ($n = 1, 2$); $\text{HO}(\text{R}_2\text{SnO})_3\text{H} \cdot \text{R}'_3\text{SnX}_2^{628,641,1027-1029}$; $(\text{R}_3\text{Sn})_2\text{O} \cdot \text{R}'_3\text{SnX}^{1030}$; $\text{R}_3\text{SnOH} \cdot \text{R}'_3\text{SnX}^{641,1031,1032}$ ($\text{R}, \text{R}' = \text{Alk}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) were described. This series can be supplemented with the $\text{Me}_2\text{SnO} \cdot \text{Me}_2\text{Sn}(\text{OH})\text{I}^{589}$ adduct. Such complexes often appeared as by-products when the syntheses of organotin compounds having a Sn–X or Sn–O bond were carried out. It is noteworthy that many solid organotin compounds having the stannoxane bond were found to be coordinated polymers rather than monomers, as hitherto considered, because their molecules were bonded by donor–acceptor (bridge) Sn–O \rightarrow Sn bonds.

Hypervalent intramolecular organotin compounds are stannatranes $\text{RSn}(\text{OCH}_2\text{CH}_2)_3\text{N}$ and dragonoides $\text{Y}(\text{CH}_2)_3\text{SnX}_3$ ($\text{Y} = \text{an atom having at least one lone electron pair, e.g. N, O, Cl}$), which appeared only in the 1970s and hence do not yet belong to history.

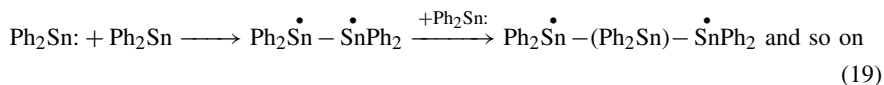
The first attempt of Zelinskii and Krapivin^{921,944} to prove the ionization of alkylhalostannanes was undertaken in 1896. By electroconductive investigations of methanolic solutions of Et_3SnI and Et_2SnI_2 they established that these compounds behaved similarly to weak electrolytes in the aqueous medium, i.e. according to the dilution law. From the second quarter of the 20th century the possible existence of organotin cations

R_3Sn^+ and R_2Sn^{2+} in solutions was raised. In the Kraus^{1013,1033,1034} (1923–1924) and Rochow^{915,924,1035} (1952–1957) laboratories the dissociation of alkylchlorostannanes in water and in organic solvents was studied extensively. The solutions of ethyl- and methylhalostannanes in water, in lower alcohols, in acetone and in pyridine displayed comparatively efficient electrolytic conduction, but their conductivity in ether, nitrobenzene and nitromethane was insignificant^{1013,1033,1034,1036}. The ionization constant of Me_3SnCl in EtOH was 10^{-5} at 25 °C¹⁰³⁴. Rochow and coworkers^{915,924} found that Me_2SnCl_2 was dissociated in water into Me_2Sn^{2+} and Cl^- . The solutions were acidic, indicating that partial hydrolysis (*ca* 10% in very dilute solutions)¹⁰³⁷ took place. According to the conductometric titration data of solutions of the organylhalostannanes Me_3SnCl , Me_2SnCl_2 , Ph_3SnCl , Ph_3SnF (as well as Ph_3MCl , where $M = Si, Ge, Pb$) they did not dissociate into ions¹⁰³⁵ in such an aprotic solvent as pure DMF.

Dissociation of Me_2SnCl_2 and Me_3SnCl and their analogs in H_2O enable the displacement of the halogen atoms in organylhalostannanes by other atoms and groups present in the aqueous medium.

The Rügheimer's⁹⁹³ ebullioscopic molecular weight measurements (1908) of $Et_3SnSnEt_3$ in ether indicated the possibility of the generation of a free organotin radical R_3Sn^{\bullet} (Section III.H). These measurements showed that the apparent molecular weight of hexaethylstannane decreased on decreasing its concentration in ether solvent. In 1925, Kraus and Session⁷⁸² achieved similar results when they found that $Me_3SnSnMe_3$ was almost completely dissociated in dilute solutions into free Me_3Sn^{\bullet} radicals. Bullard, in his doctoral dissertation (1925), found that $Me_3SnSnEt_3$ was formed from an equimolecular mixture of $Me_3SnSnMe_3$ and $Et_3SnSnEt_3$ in boiling benzene solution. In his opinion this indicated the intermediacy of Me_3Sn^{\bullet} and Et_3Sn^{\bullet} free radicals. Stable free radicals R_3Sn^{\bullet} with $R = CH(Me_3Si)_2$ were first obtained by Lappert^{514,1038} by photochemical disproportionation of $[(Me_3Si)_2CH]_2Sn$ at the end of the last century.

The history of organic hypovalent (divalent) tin derivatives R_2Sn seemed as old as the rest of the chemistry of organotin compounds, but this is not so because almost all compounds with the structure R_2Sn synthesized for over 100 years were the cyclic oligomers or polymers of tetravalent tin (see Section III.H), but not the monomers as originally thought. Old arguments which supported the monomeric structures of these compounds, such as the facile addition reactions of halogens, hydrohalic acids, oxygen and sulfur to R_2Sn , were in fact due to Sn–Sn bond cleavage. Nevertheless, many investigators in the past encountered monomeric diorganylstannylenes R_2Sn , which were the intermediates in reactions developed by them. Organotin compounds $R_2Sn=Y$ ($Y = SnR_2^{516}, CR_2, OS, Se^{523}$ etc.), having three-coordinated Sn atom, bonded by a double bond atom or to another Sn element, can be considered as the hypovalent tin derivatives. However, they also appeared only at the end of the past century and their historical development lies beyond the scope of this chapter. In 1926 Chambers and Scherer⁶⁶², and then Schmitz-DuMont and Bungard¹⁰³⁹ observed the formation of the first representative of these labile compounds, i.e. diphenylstannylene Ph_2Sn , in the thermal dissociation of diphenylstannane Ph_2SnH_2 . However, Krause and Becker⁷⁸¹ were the first who had Ph_2Sn in their hands in 1920. In 1943, Jensen and Clauson-Kass⁹⁸⁴ confirmed this fact when they showed that freshly prepared (according to the Krause) diphenylstannylene was monomeric and that it slowly polymerized on storing to give the pentamer $(Ph_2Sn)_5$, hexamer and higher oligomers. Diphenylstannylene, which was diamagnetic in all the polymerization stages, maintained a constant value of its dipole moment (1.0 D). This gave rise to the suggestion that, when formed as intermediates, the oligomers were biradicals obtained according to equation 19.



The synthesis of stable diorganylstannylenes, the true divalent organotin derivatives, was carried out only in the second half of the 20th century^{68,97,105,508,514,1038,1040–1043}. The first stable diorganylstannylene (named ‘homoleptic’¹⁰⁴⁰) $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ appeared in the Lappert laboratory^{1044,1045} after 1975. However, these investigations¹⁰⁴⁰ and those about stable free radicals $\text{R}_3\text{Sn}\cdot$ ^{58,516} lie beyond the scope of this chapter.

J. Biological Activity

Among investigations into the biological activities of organometallic compounds, those of organotin derivatives are highly important^{91,99,1046–1049}, being comparable only with those on the biological activity of mercury and lead compounds. The majority of investigations into the organotin compounds were related to their toxicity that influenced the working process and the experimentalist’s health. In 1951 there were four cases of poisoning with Me_4Sn and Et_4Sn which were reported to result from careless treatment of these substances in the laboratory¹⁰⁵⁰.

Already in 1853, Frankland⁴⁵ paid attention to the toxicity of organotin compounds. But the first experimental investigations of their toxicity were conducted by White^{1051,1052} in 1881 and 1886. He found that, unlike inorganic tin salts, triethylacetoxystannane was highly toxic for frogs, rabbits and dogs. In 1886, Ungar and Bodländer¹⁰⁵³ studied the toxicity of some organotin compounds on mammals.

Only forty years later did the investigations on toxicity and biological activity of organotin compounds restart in 1926 due to Hunt¹⁰⁵⁴. Collier¹⁰⁵⁵ found in 1929 that the toxicity of aromatic organotin compounds increased in the order: $\text{Ph}_4\text{Sn} < \text{Ph}_3\text{SnSnPh}_3 < \text{Ph}_3\text{SnPr} < \text{Ph}_3\text{SnBr}$. According to Lesbre and coworkers¹⁰⁵⁶ aliphatic tin derivatives are more toxic than the aromatic ones, and R_3SnX is more toxic than R_2SnX_2 and R_4Sn ($\text{R} = \text{alkyl}$). In 1954–1955 the toxic action of the organotin compounds on warm-blooded animals was determined^{1056,1057}. It was found that in the $\text{Et}_{4-n}\text{SnX}_n$ series the toxicity of the compounds with $n = 1$, i.e. Et_3SnX ($\text{LD}_{50} = 5\text{--}10 \text{ mg kg}^{-1}$), was the highest. The Et_2SnX_2 poisoning was reduced by 2,3-dimercaptopropanol (dimercaptol-BAL), demonstrating an equal toxic action of R_2SnX_2 to that of organic mercury and lead compounds. At the same time, antagonists for Et_3SnX were not found. Seifter¹⁰⁵⁸ (1939), Gilman¹⁰⁵⁹ (1942), Glass and coworkers¹⁰⁶⁰ (1942) and McCombie and Saunders⁹⁷¹ (1947) were involved in the search of organotin compounds as war poisoning substances during World War II. As a result of their investigations the structure–toxicity relationship of organotin compounds was established. Trialkylstannane derivatives R_3SnX , $\text{R} = \text{Me, Et}$ stimulated progress of the momentum reversible paralysis and retarded encephalopathy. These compounds and also R_2SnX_2 derivatives, $\text{R} = \text{Me, Et, Pr, Bu}$ possessed dermato-vesical, lachrymatorial and skin-irritating influence. However, none of them was employed as war poisoning agents. In 1940–1942, toxicological studies of the organotin compounds started at the Medical Research Council in Great Britain and in Toulouse University. In 1955 Stoner, Barnes and Duff¹⁰⁵⁷ studied the toxicity and biological activity of the $\text{R}_{4-n}\text{SnX}_n$ ($\text{R} = \text{Alk}$; $n = 0\text{--}3$) series. They found that the influence of Et_3SnX and Et_2SnX_2 was quite different and that only the toxic effect of the latter compound was suppressed by 2,3-dimercaptopropanol. The results of investigations of the influence of tetraalkylstannane under intravenous, intramuscular, oral and intraperitoneal infusion¹²⁵ were summarized in

Meynier's doctoral dissertation (1955) and published in 1956¹⁰⁶¹. In 1955–1959 a series of physiological investigations of organotin compounds and a mechanistic study of their influence on laboratory animals were carried out^{923,1061–1066}.

In 1950 in Utrecht intensive investigations of toxicity and fungicidal activities of organotin compounds begun under van der Kerk supervision^{88,713,1067}. First, the fungicide activities of $\text{Et}_{4-n}\text{SnX}_n$ ($n = 0-4$) were investigated and it was found that Et_3SnCl ($n = 1$) possessed the maximal fungicide action. Compounds R_4Sn , R_2SnX_2 and RSnX_3 , having different R and X substituents, were less active in comparison with R_3SnX .

Further studies of the fungicide activities of compounds R_3SnX showed that the activity was almost independent of the type of the substituent X. This led to the conclusion that toxicity of R_3SnX was conditioned by the R_3Sn^+ ion or probably by the undissociated R_3SnOH . In contrast, the R substituents affected strongly the fungicidal properties of the R_3SnX ($\text{X} = \text{OCOMe}$) series. This effect was maximal at $\text{R} = \text{Pr}$, Bu . Further investigation of $\text{R}'\text{R}_2\text{SnX}$ ($\text{R} = \text{Me}$, Et ; $\text{R}' = \text{C}_n\text{H}_{2n+1}$; $n = 2-12$) derivatives showed that the fungicide activity was dependent only on the total number of carbon atoms in the three-alkyl groups bonded to the tin atom. The maximal activity was achieved when this number was 9–12.

In 1938 it was found that organotin derivatives of proteins and nucleoproteins and the products of their hydrolysis could be used to treat some skin and blood diseases^{1068,1069}.

Kerr¹⁰⁷⁰ and Walde¹⁰⁷¹ found that $\text{Bu}_2\text{Sn}(\text{OCOC}_{11}\text{H}_{23})_2$ was a very effective medication against some intestinal worm infections of chickens. Later, this medication was patented.

Physicians called attention to the effective antimicrobial action of organotin compounds in the middle of the last century. In 1958, 'Stalinon', a medical preparation consisting of diethyldiiodostannane and isolinolenic acid esters¹⁰⁷², was produced in France for the treatment of staphylococcus infections. Hexabutyldistannoxane in combination with formaldehyde¹⁰⁴⁶ was used as a remedy against *Staphylococcus aureus*.

The insecticide action of organotin compounds attracted attention in the first half of the 20th century. In 1929 and 1930 a great number of compounds $\text{R}_{4-n}\text{SnX}_n$ were patented as a remedy against moth^{1073–1075}. In 1952 a patent on the application of trialkylchlorostannanes as insecticides was issued¹⁰⁷⁶. In 1946, some organotin compounds were patented as the active components of anti-overgrowing coatings¹⁰⁷⁷. Somewhat later the stable bioprotective organotin coatings were developed on the basis of monomers of the $\text{R}_3\text{SnS}(\text{CH}_2)_n\text{Si}(\text{OR}')_3$ type¹⁰⁷⁸.

K. Practical Use

In the second half of the 20th century organotin compounds found extensive applications in different technological fields^{50,125,151} and in agriculture^{125,1046,1079}. In 1980 the annual world production of organotin compounds was 35,000 tons¹⁵² and 28,000 tons of metallic tin¹⁰⁸⁰ were used as the precursor.

The practical application of the organotin compounds started with the fundamental investigations of Yngve, who found that several organotin compounds were excellent photo- and thermo-stabilizers of polyvinyl chloride and other chlorinated polymers, and received a patent in 1940¹⁰⁸¹. For the next several years, many other organotin compounds were patented^{1082–1085}. Compounds of the types $\text{Bu}_2\text{Sn}(\text{OCOR})_2$ and $\text{Bu}_2\text{Sn}(\text{OCO})_2\text{R}'$ ($\text{R}' = \text{divalent organic radical, preferably unsaturated}$) were found to be the best stabilizers. Just up to 1960, 82 patents, cited in reviews^{125,675} and in several articles^{1086–1090}, were devoted to PVC organotin stabilizers. In 1953, Kenyon¹⁰⁹¹ first started to investigate the mechanism governing the influence of the organotin stabilizers. In 1953–1958

organotin compounds were offered as stabilizers for liquid chlorinated dielectrics^{1092,1093}, chloro-containing dye stuffs for rubber¹⁰⁹⁴ and polystyrene^{1095,1096} and as inhibitors of corrosion¹⁰⁹⁷. In 1949, based on Hart's¹⁰⁹⁸ investigations, a patent for the use of tribenzylalkylstannanes $(\text{PhCH}_2)_3\text{SnR}$ as antioxidants for protecting rubbers from cracking was issued. In 1954–1959 a series of different R_2SnX_2 and R_3SnX compounds which were identical to already known polyvinyl chloride stabilizers¹⁰⁶⁴ were patented for similar use.

Patents dealing with possible practical use of organotin compounds as components for catalytic systems for polymerization of olefins^{125,675} appeared during the same period of time. The investigations of chemists and biologists from Utrecht⁷¹³ proposed the practical use of organotin compounds as biocides (fungicides¹⁰⁹⁹, insecticides¹¹⁰⁰) and biocide coatings and impregnations^{1101,1102}. Compounds Et_3SnX ($\text{X} = \text{OH}$, OCOMe) were found to effectively suppress ordinary types of fungus which damaged wood. Consequently, they recommended these compounds for practical use, for example^{1047,1103}, to protect timber in mines from biodegradation, and against fabric damage (cotton, jute) by insects and fungus. Further, the R_3SnX compounds were proposed as highly effective means against plant diseases (pesticides)¹⁰⁹⁹, for the bioprotection of hemp, sisal ropes¹¹⁰⁴, and paper¹⁰⁴⁷, as insecticides¹¹⁰⁵ and as fungistatic agents for dyes¹¹⁰⁶.

IV. ORGANOLEAD COMPOUNDS

A. Introduction

Organolead compounds came into the world in 1852–1853, i.e. at the same time as organotin chemistry was born. The Swedish chemist Löwig, mentioned extensively in section III as one of the founders of organotin chemistry, is also the father of organolead compounds. He had in his hands for the first time simple representatives of organolead compounds such as $\text{Et}_3\text{PbPbEt}_3$ and the triethylplumbane derivatives Et_3PbX ($\text{X} = \text{I}$, Br , Cl , OH , NO_3 , 0.5SO_4)^{42,43,1107}. In the 19th century and at the beginning of the 20th century, the development of the chemistry of organolead compounds was not intensive, although its basis was founded at this period. Only in the years 1915–1925 did organolead chemistry start to develop more quickly due to the efforts of Grüttner and Krause^{674,1108–1119} and Krause and coworkers^{186,781,814,833,1120–1127}. The systematic investigations showed that organolead compounds could be divided into two main classes: derivatives of tetravalent lead ($\text{R}_{4-n}\text{PbX}_n$) and divalent lead (R_2Pb). Gilman's investigations carried out in 1937–1952 (for reviews see References 1128 and 1129) contributed significantly to the chemistry of organolead compounds. His investigations led to the development of metalloorganic lead derivatives, such as Ph_3PbLi , which turned out to be an important synthon for the synthesis of different organolead compounds. The studies of Kocheshkov and coworkers^{54,156,1130–1134}, who were the first to study the possible existence of aryltriacyloxyplumbanes $\text{RPb}(\text{OCOR}')_3$, were unknown until 1950.

What had Löwig done and what would follow from his work? Among the organic derivatives of the heavy elements of Group 14 only the organolead compounds attracted the least attention. This is evident by the number of publications in this field, which totaled 350^{741,1135,1136} up to the middle of the 20th century (of which only 20 appeared in the 19th century) and 420 publications appeared up to 1963^{109,1129}. Due to their high toxicity, low thermal and chemical stability, and the similarity of the methods for their synthesis and chemical properties with those of their isostructural tin compounds, there was in general less interest in the organolead compounds. In addition, there was a dominant opinion that the fundamental investigations of organolead compounds could not lead to new developments in comparison with organotins. Nevertheless, the chemistry of tetraalkylplumbanes led to two important discoveries in the 1920s, namely the

thermal generation of free radicals by Paneth and Lautsch in 1929–1931^{1137–1139} and the discovery of antiknock additives for motor fuels by Midgley and coworkers in 1923¹¹⁴⁰.

B. Synthesis from Metallic Lead and its Alloys

In 1852, Löwig¹¹⁰⁷ obtained hexaethyldiplumbane $\text{Et}_3\text{PbPbEt}_3$, initially confused with Et_4Pb , by heating ethyl iodide with a lead–sodium alloy. In the 20th century this became the predecessor of the industrial synthesis of Et_4Pb . Following Löwig, Polis¹¹⁴¹ (1887), Ghira^{1142,1143} (1893, 1894), Tafel¹¹⁴⁴ (1911), Calingaert¹¹⁴⁵ (1925), Fichter and Stein¹¹⁴⁶ (1931), Goldach¹¹⁴⁷ (1931) and others^{47,54,110,1129} studied the reaction of lead–sodium alloy with organic halides. Tafel¹¹⁴⁴ and Ghira^{1142,1143} established the correct structure of the substance obtained by Löwig^{42,43,1107}. Kraus and Callis⁶⁴³ found the optimal conditions for the industrial production of Et_4Pb , namely the reaction of Pb–Na alloy with EtCl , which was cheaper and more readily available than EtI , which proceeded according to equation 20.



Consequently, 3/4 of the lead was recovered and could be used further. In the laboratory this method had only limited use. In particular, it was used by Calingaert and coworkers¹¹⁴⁸ and Saunders and coworkers^{1149,1150} to obtain R_4Pb with $\text{R} = \text{Me}, \text{Et}, \text{Pr}, i\text{-Bu}$ in 1948 and 1949, respectively. From 1927^{1151,1152} many dozens of patents appeared following the investigations of Kraus and Callis, to protect the method for preparing the R_4Pb ($\text{R} = \text{Me}, \text{Et}$) by the reaction of Pb–Na alloy (sometimes with addition of K, Li, Mg, Ca) with RCl , RBr and $(\text{EtO})_2\text{SO}_2$ under different conditions^{47,109,110}. It is impossible to demonstrate all of them here, but we point out that one of the first patents for the preparation of Et_4Pb was granted to Kraus in 1928¹¹⁵³. Even in 1950 patents for the preparation of Et_4Pb from lead alloys with Mg^{1154,1155} and Ca¹¹⁵⁶ were published. Hence the reaction of alkyl halides with lead–sodium alloy, discovered by Löwig^{42,43,1107} opened the way for the industrial production of tetraethyllead. A total of 166,000 tons (1/6 of the US lead production) was used to produce tetraethyllead¹¹⁵⁷.

Already in 1887, Polis¹¹⁴¹ obtained tetraphenylplumbane Ph_4Pb by the reaction of PhBr with Pb–Na alloy in the presence of ethyl acetate. Calingaert¹¹⁴⁵ found that the reaction of alkyl halides with Pb–Na alloy was promoted also by water and by the other compounds, and hydrogen was formed in the reaction with the alloy. We note that in 1853 Cahours¹¹⁵⁸ found that metallic lead reacted at a low rate with EtI on heating to give unidentified organolead compounds. Although this was not of any practical interest, metallic lead, but not its alloy, was used successfully for the synthesis of R_4Pb . In 1911, Tafel¹¹⁴⁴ showed that the electrochemical reduction of acetone on lead cathode in sulfuric acid solution led to formation of $i\text{-Pr}_4\text{Pb}$. In 1925, the electrochemical synthesis of tetraalkylplumbanes from alkyl bromides and iodides by using a lead cathode was patented^{1159,1160}. The intermediate in this process was dialkylplumbylene, which was rapidly transformed into tetraalkylplumbane at the high temperature of the cathode electrolyte. In 1942, Nad' and Kocheshkov¹¹⁶¹ found that the reaction of Ar_2PbCl_2 with metallic lead or Pb–Na alloy in boiling xylene led to Ar_3PbCl and PbCl_2 .

C. Metalloorganic Approaches to Organolead Compounds

Historically, the first metalloorganic method for the synthesis of organolead compounds was based on the use of zinc dialkyls. It was not surprising that the method was first

used by Frankland and Lawrence^{591,1162}, who used zinc dialkyl in other reactions. In 1859 they synthesized R_2PbCl_2 by the reaction of $PbCl_2$ with R_2Zn ($R = Me, Et$). In 1859 Buckton^{603,604,1163} obtained R_4Pb by the reaction of $PbCl_2$ with R_2Zn ($R = Me, Et$). The effort of Tafel¹¹⁴⁴ to synthesize $(i-Pr)_4Pb$ in 1911 failed. In 1925, Meyer¹¹⁶⁴ described the organozinc synthesis of Et_4Pb from $PbCl_2$.

The reactions of lead dihalides with organomagnesium compounds then became widely used and a convenient laboratory method. Unlike organic derivatives of silicon, germanium and tin, which were usually prepared from $MHal_4$ ($M = Si, Ge, Sn$) according to the Grignard method, the lead tetrahalides $PbHal_4$ could not be used for this purpose because of their extraordinary instability. The organomagnesium synthesis of organolead compounds was first applied by Pfeiffer and Trüskier¹¹⁶⁵ in 1904 and then by Möller and Pfeiffer in 1916¹¹⁶⁶. They obtained both a tetraalkyl- and a tetraarylplumbane R_4Pb ($R = Et, Ph$) by the reaction of organylmagnesium halides $RMgX$ with $PbCl_2$. Metallic lead was the by-product of the reaction. Later, Ph_4Pb was similarly synthesized in the laboratories of Krause¹¹²⁴ (1925), Gilman^{1167,1168} (1927 and then 1939), Kocheshkov¹¹⁶⁹ (1937) and others. This method was not suitable for the preparation of some other tetraarylplumbanes; e.g. $Ar_3PbPbAr_3$ ^{1120,1170,1171} was the main product of the reaction of $ArMgX$ with $PbCl_2$. Krause and Reissaus¹¹²² managed to carry out the reaction of $PhMgBr$ with $PbCl_2$ in such a way that the main reaction product was $Ph_3PbPbPh_3$. In 1914, Grüttner and Krause^{674,1121} succeeded in obtaining tetraacyclohexylplumbane according to the Grignard method. In 1916–1918, Grüttner and Krause^{1110,1114,1115,1117} used Grignard reagents for the synthesis of R_4Pb with $R = Me, Et, Pr, i-Pr, i-Bu, i-Am$. In 1916, Möller and Pfeiffer¹¹⁶⁶ were the first to use organylhaloplumbanes in the Grignard reaction. They obtained Ph_2PbEt_2 by the reaction of Ph_2PbBr_2 with $EtMgBr$. In 1919, Krause and Schmitz⁸¹⁴ synthesized mixed tetraorganylplumbanes $(1-C_{10}H_7)_2PbR_2$ ($R = Et, Ph$) by the Grignard method. It was also found that in the reaction of $2,5-Me_2C_6H_3MgBr$ with $PbCl_2$ only $(2,5-Me_2C_6H_3)_3PbPb(C_6H_3Me_2-2,5-C_6H_3-2,3-Me_2)_3$ was obtained, but not tetra-*p*-xylylplumbane. The reaction of $PbCl_2$ with $2-MeC_6H_4MgBr$ proceeded analogously¹¹²². There were no doubts that such a result was due to the steric hindrances. In 1928 the organomagnesium method of the synthesis of Et_4Pb was patented^{1172–1175}. The use of the Grignard reagent enabled one to obtain compounds of the types R_3PbPbR_3 , R_2Pb , $R_{4-n}PbR'_n$ ($n = 0–3$) and $R_2R'R''Pb$ ¹¹²⁹ from PbX_2 . Compounds such as 1,1-diorganylplumbacycloalkanes belong to this group, and the first representative 1,1-diethylplumbacyclohexane $Et_2Pb(CH_2)_5-c$ was obtained by the reaction of Et_2PbCl_2 with $BrMg(CH_2)_5MgBr$ by Grüttner and Krause¹¹¹² in 1916. Tetrabenzylplumbane, which is extremely easily oxidized by air (sometimes with inflammation), was first synthesized by Hardtmann and Backes⁷¹⁰ by the Grignard method and two years later by Krause and Schlöttig⁸³³ and then by Lesbre¹¹⁷⁶. Unstable tetravinylplumbane was first synthesized by the action of the Norman reagent $CH_2=CHMgX$ ($X = Cl, Br$) on $PbCl_2$ or on $Pb(OCOMe)_2$ by Juenge and Cook¹¹⁷⁷ in 1959. As early as in 1916, Grüttner and Krause¹¹¹⁰ and Möller and Pfeiffer¹¹⁶⁶ observed that in the reaction of the Grignard reagent with $PbCl_2$ the reaction mixture became red. This was explained by the intermediate formation of colored diorganylplumbylenes R_2Pb . However, all attempts to isolate dialkylplumbylenes from the solutions failed¹¹⁴⁵. In contrast, several publications^{984,1122,1178,1179} were devoted to diarylplumbylenes Ar_2Pb , before 1961. In 1922, Krause and Reissaus¹¹²² isolated the red powder-like Ar_2Pb together with $Ar_3PbPbAr_3$ from the reaction products of $PbCl_2$ with $ArMgBr$ ($Ar = Ph, 4-MeC_6H_4$) at $0^\circ C$.

In 1932, Austin⁶⁸⁰ used for the first time organolithium compounds for the synthesis of organoleads. He reported that the reaction of $ArLi$ with $PbCl_2$ led to Ar_2Pb . Further heating of the latter led to products such as Ar_4Pb , $Ar_3PbPbAr_3$ and Pb ^{680,1180,1181}.

However, in 1941 Bindschadler and Gilman¹¹⁸² concluded that the reaction proceeded in another way. The reaction mixture of PbCl_2 with PhLi at -5°C was not red colored due to Ph_2Pb , and free lead was not isolated. In addition, boiling of $\text{Ph}_3\text{PbPbPh}_3$ in an ether-toluene mixture did not result in the formation of Ph_4Pb . Based on these facts they concluded that $\text{Ph}_3\text{PbPbPh}_3$, Ph_3PbLi and, finally, Ph_4Pb ¹¹⁸² were consequently formed in the reaction. Austin^{680,1180} obtained R_3PbAr and R_2PbAr_2 ($\text{R} = \text{Ar}$) by the reaction of ArLi with R_3PbCl and R_2PbCl_2 , respectively. In 1940, Gilman and Moore¹¹⁸³ used the reaction of ArLi with $\text{R}_{4-n}\text{PbX}_n$ ($n = 1, 2$) for the synthesis of R_3PbAr and R_2PbAr_2 . Austin^{680,1180} in 1932 obtained optically active $\text{PrPh}(2\text{-MeC}_6\text{H}_4)\text{Pb}(\text{C}_6\text{H}_4\text{OOct-}i)$ by the reaction of $(i\text{-OctOC}_6\text{H}_4)\text{Li}$ with optically active $\text{PrPh}(2\text{-MeC}_6\text{H}_4)\text{PbX}$. Talalaeva and Kocheshkov^{666,667} were the first to describe the reaction of PhLi with lead powder which resulted in low yield of Ph_4Pb and metallic Li . Replacement of lead with its amalgam increased the output of the products and reduced the time of the reaction⁶⁶⁷. In 1950, Gilman and Jones¹¹⁸⁴ found that the reaction of MeLi with PbI_2 and MeI resulted in Me_4Pb formation. Metallic lead and Me_2PbI_2 were the intermediate products of the reaction. The reaction of PbCl_2 with ArLi and with the appropriate aryl iodide was carried out analogously and led to Ar_4Pb ($\text{Ar} = \text{Ph}$, $4\text{-Me}_2\text{NC}_6\text{H}_4$)^{239,1185}.

In 1941, in the Gilman laboratory, triphenylplumbyllithium was first synthesized by the addition of excess PhLi to PbCl_2 in ether at -10°C ¹¹⁸². In 1951, Gilman and Leeper³¹⁶ developed another synthesis of triphenylplumbyllithium Ph_3PbLi by the reaction of $\text{Ph}_3\text{PbPbPh}_3$ with metallic Li . In 1917, Schlenk and Holtz¹¹⁸⁶ and later Hein and Nebe¹¹⁸⁷ (1942) found that metallic Na cleaved R_4Pb in ether solvent. In 1938, Calingaert and Soroos¹¹⁸⁸ found that alkyhaloplumbanes reacted with a stoichiometric amount of Na in liquid ammonia to give hexaalkyldiplumbanes R_3PbPbR_3 ($\text{R} = \text{Me}$, Et). Gilman and Bailie^{791,1170}, Foster and coworkers¹¹⁸⁹ and Bindschadler¹¹⁹⁰ observed that R_3PbPbR_3 was formed by the reaction of Na with R_3PbX ($\text{R} = \text{Alk}$, Ph ; $\text{X} = \text{Cl}$, Br) in ammonia, and that the dark-red solution of R_3PbNa was formed. In 1941, Bindschadler¹¹⁹⁰ succeeded in obtaining R_3PbNa by the cleavage of R_4Pb by sodium in liquid ammonia. The ease of the R-Pb bond cleavage was found to decrease in the following order for R : $\text{CH}_2\text{CH}=\text{CH}_2 > i\text{-Bu} > \text{Bu} > \text{Et} > \text{Me} > \text{Ph} > 4\text{-Me}_2\text{NC}_6\text{H}_4$. Thus, for example, Et_2PhPbNa ¹¹⁹⁰ was formed from the reaction of sodium with Et_3PbPh in the liquid ammonia. However, the best way for obtaining Et_3PbNa became the cleavage of Et_4Pb by sodium in liquid ammonia. Ph_3PbNa was prepared similarly from $\text{Ph}_3\text{PbPbPh}_3$ ¹¹⁹⁰. In 1951, Gilman and Leeper³¹⁶ found that $\text{Ph}_3\text{PbPbPh}_3$ was cleaved by K , Rb , Ca , Sr , Ba in liquid ammonia. In 1926, Hardmann and Backes⁷¹⁰ patented the method of tetraalkylplumbane preparation by the reaction of PbCl_2 and RX with Na in toluene.

The transformations of compounds Ph_3PbM ($\text{M} = \text{Li}$, Na) and their possible use for synthetic purposes started to develop in 1939, but the basic investigations in this field were carried out after 1960.

In 1939, Gilman and Bailie^{791,1170} demonstrated that the reaction of Ar_3PbNa with PhCH_2Cl or Ph_3CCl led to Ar_3PbR ($\text{R} = \text{CH}_2\text{Ph}$, CPh_3). In 1950 in Gilman's laboratory¹¹⁹¹ Et_3PbNa , which turned out to be more reactive than Ph_3PbNa , was introduced as a reagent in the reaction with organic halides. The reaction of Et_3PbNa with PhCH_2Cl was 'abnormal' and led mainly to formation of stilbene. In 1959, Et_3PbNa was used for the synthesis of $\text{Et}_3\text{PbCH}=\text{CHPh}$ by Glockling and Kingston¹¹⁹².

Triphenylplumbyllithium was introduced into synthetic practice by Gilman and Summers^{239,1193} only in 1952. In 1952, D'Ans and coworkers⁹⁸⁶ used Ph_3PbLi to obtain fluorenyllithium. In 1932, Shurov and Razuvaev¹¹⁹⁴ studied the transfer of phenyl radicals, formed by the thermolysis of Ph_nM ($\text{M} = \text{metal}$) to another metal atom, which formed

more thermally stable phenyl derivatives. They found that the reaction of Ph_4Pb with Sn led to the formation of Ph_4Sn and Pb at 300–375 °C.

Shurov and Razuvaev¹¹⁹⁴ tried, but failed to prepare phenyl derivatives of lead by the reaction of metallic lead with Ph_2Hg , as well as with Ph_3Bi . Aromatic mercury compounds were first used for the synthesis of organolead compounds in 1932 when Austin¹¹³⁶ obtained Ph_3PbCl by the reaction of Ph_2Hg with Ph_2PbCl_2 , but he failed when synthesizing Ph_4Pb and $(p\text{-MeC}_6\text{H}_4)_2\text{PbCl}_2$ by this method. In 1934, Nesmeyanov and Kocheshkov⁸¹³ reported that the reaction of Ph_4Pb with HgCl_2 led to Ph_3PbCl or Ph_2PbCl_2 along with PhHgCl . In 1942, Nad' and Kocheshkov¹¹⁶¹ found that the reaction of Ar_2Hg with tetraacetoxyplumbane $\text{Pb}(\text{OCOMe})_4$ proceeds easily at room temperature in CHCl_3 , to give $\text{Ar}_2\text{Pb}(\text{OCOMe})_2$. The same reaction with Et_2Hg took three months. These authors first used this reagent for the synthesis of organolead compounds. This reaction enabled one to obtain otherwise almost inaccessible compounds, like Ar_2PbX_2 having reactive substituents in the aromatic ring. The reaction of tetraacetoxyplumbane with $(\text{ClCH}=\text{CH})_2\text{Hg}$ was used by Nesmeyanov and coworkers^{1195,1196} for the preparation of $(\text{ClCH}=\text{CH})_2\text{Pb}(\text{OCOMe})_2$ in 1948. In 1956–1964, the reaction of Ar_2Hg with $\text{Pb}(\text{OCOR})_4$ was used extensively for the synthesis of $\text{ArPb}(\text{OCOR})_3$ in Kocheshkov's laboratory^{1197–1200}.

Hein and Klein¹²⁰¹ obtained hexaethyldiplumbane by the reaction of an alkaline solution of Et_3PbCl with aluminum powder. In 1959, Razuvaev, Vyazankin and coworkers^{1202,1203} showed that Et_2Pb was formed in this reaction along with $\text{Et}_3\text{PbPbEt}_3$. This reaction was a usual reduction process and organoaluminum compounds were not its intermediate products. The use of the reaction for the synthesis of organolead compounds began only in 1957. Its use was complicated by the fact that both aluminum alkyls and AlCl_3 , which are obtained by the reaction of the organoaluminum compounds with PbCl_2 , cleaved the C–Pb bond in the formed organolead compounds⁷³¹. Therefore, the reaction of R_3Al with PbCl_2 had to be carried out in the presence of alkali metal halides, which reacted with AlCl_3 or when PbCl_2 was replaced by $\text{Pb}(\text{OCOMe})_2$ ⁷³¹ or PbF_2 (when the inert AlF_3 was formed). In 1957, Jenker¹²⁰⁴ used this method. In 1957–1958, the methods for the preparation of tetraalkylplumbanes by the reaction of PbCl_2 with LiAlEt_4 ¹²⁰⁵ or with equivalent amounts of R_3Al and RI ¹²⁰⁶ were patented.

D. Nonorganometallic Approaches to the Formation of a C–Pb Bond

The Nesmeyanov reaction based on a decomposition of double aryldiazonium salts by the powdered metals had little importance for the synthesis of organolead compounds because of the low yields of the products¹²⁰⁷. In 1936 Kocheshkov, Nesmeyanov and Gipp prepared Ph_3PbCl by the decomposition of $\text{PhN}_2\text{Cl} \cdot \text{PbCl}_2$ with zinc powder in ether medium¹²⁰⁸. Ph_2PbCl_2 was prepared when copper powder and acetone were used in the reaction. In both cases the yields of phenylchloroplumbanes were small. In 1945 Nesmeyanov, Kocheshkov and Nad'¹²⁰⁹ succeeded in obtaining Ph_4Pb in 16.5% yield by the decomposition of PhN_2BF_4 by powdered pure lead at 6 °C. When the alloy of lead with 10% Na was used instead, the yield of Ph_4Pb increased to 30%¹¹¹⁰. Tetra-*p*-xylylplumbane $(4\text{-MeC}_6\text{H}_4)_4\text{Pb}$ was synthesized analogously in 18% yield. Aliphatic diazo compounds were originally used for the synthesis of organotin compounds by Yakubovich^{1210,1211} in his laboratory in 1950 and 1952. He showed that Et_3PbCl and Et_2PbCl_2 reacted with diazomethane in the presence of powdered bronze to give $\text{Et}_3\text{PbCH}_2\text{Cl}$ and $\text{Et}_2\text{Pb}(\text{CH}_2\text{Cl})\text{Cl}$ or $\text{Et}_2\text{Pb}(\text{CH}_2\text{Cl})_2$, respectively.

In 1960, Becker and Cook¹²¹² found that the reaction of trialkylplumbanes R_3PbH ($\text{R} = \text{Me}, \text{Et}$) with diazoethane at –80 °C in ether led to R_3PbEt in a low yield.

The hydroplumbylation reaction (addition of organolead hydrides to multiple bonds)⁵³ was first carried out by Becker and Cook¹²¹². They showed that Me_3PbH added to ethylene in diglyme at 0°C under pressure of 17–35 atm to give Me_3PbEt in 92% yield. Further investigations were performed by Neumann and Kühlein¹²¹³ and by Leusink and van der Kerk¹²¹⁴ in 1965. The addition of R_3PbOH or $\text{R}_3\text{PbOCOR}'$ to ketene, which was studied only in 1965, was of specific interest¹²¹⁵.

In 1958, Panov and Kocheshkov¹²¹⁶ found another route to the formation of the C–Pb bond, namely the interaction of tetraacyloxyplumbanes with aromatic and heteroaromatic compounds (the plumbylation reaction). They showed that the reaction of thiophene with $\text{Pb}(\text{OCOR}'-i)_4$ at room temperature during 10 days led to unstable $\text{RPb}(\text{OCOR}')_3$ ($\text{R} = 2\text{-thienyl}$; $\text{R}' = i\text{-Pr}$), which was disproportionated to $\text{R}_2\text{Pb}(\text{OCOR}')_2$ and $\text{Pb}(\text{OCOR}')_4$.

Alkylhaloplumbanes Et_3PbX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were synthesized by Löwig^{42,43,1107} in 1852–1853. He found that the evaporation of an alcoholic solution of $\text{Et}_3\text{PbPbEt}_3$ (formed from EtI and a $\text{Pb}\text{--Na}$ alloy) resulted in the formation of bis(triethylplumbyl)carbonate $(\text{Et}_3\text{Pb})_2\text{CO}_3$ and Et_3PbOH . Treatment of the products with hydrohalic acids gave Et_3PbX , $\text{X} = \text{Cl}, \text{Br}, \text{I}$. Analogously, the treatment of the above products with HNO_3 and H_2SO_4 resulted in the formation of Et_3PbNO_3 and $(\text{Et}_3\text{Pb})_2\text{SO}_4$, respectively.

In 1860, Klippel^{1217,1218} obtained a series of triethylacyloxyplumbanes Et_3PbOCOR with $\text{R} = \text{H}, \text{Me}, \text{Pr}, \text{Ph}$, as well as the corresponding oxalates, tartrates, cyanides and cyanates.

E. Cleavage of the C–Pb and Pb–Pb Bond

Among the C–Pb bond cleavage reactions, thermo- and photo-induced homolytic cleavage is of special theoretical and practical interest.

As early as 1887 Polis¹¹⁴¹ observed that Ph_4Pb decomposed at 300°C to free metallic lead. In 1927, Zechmeister and Csabay¹²¹⁹ showed that the reaction occurred even at 270°C to give biphenyl. Thermal decomposition of Ph_4Pb was studied thoroughly by Razuvaev, Bogdanov and Koton in 1929–1934^{1220–1224}. It was also shown that the thermolysis of tetraphenylplumbane at 200°C under normal pressure or at 175°C in ethanol under autogenic pressure resulted in metallic lead and biphenyl. The process was catalyzed by metals, which decreased the initial decomposition temperature to 150°C . The catalysis by the metal decreased in the order: $\text{Pd} > \text{Au} > \text{Ag} > \text{Ni}$. Dull and Simons¹²²⁵ (1933) showed that thermolysis of Ph_4Pb gave benzene, biphenyl and terphenyl. The ratio of the products was temperature-dependent. In 1933, Dull and Simons¹²²⁶ found that the thermolysis of Ph_4Pb in the presence of evaporated mercury involved the formation of Ph_2 and Ph_2Hg , indicating the intermediate formation of phenyl radicals. Krause and Schmitz in 1919 found that the thermal decomposition of Ph_3PbEt gave lead at 235°C i.e. at a lower temperature than that for Ph_4Pb ⁸¹⁴. The data indicated that replacement of the aryl with an alkyl substituent decreased the thermolysis temperature of tetraorganylplumbanes.

From 1929, the Paneth^{1137–1139,1227} discovery, was published, that the thermal decomposition of lower tetraalkylplumbanes R_4Pb ($\text{R} = \text{Me}, \text{Et}$) at *ca* 400°C led to metallic lead and free CH_3^\bullet or $\text{C}_2\text{H}_5^\bullet$ radicals, respectively. These free radicals transformed the smooth surface of the metals $\text{Pb}, \text{Zn}, \text{Cd}, \text{As}$ and Sb into the corresponding metal alkyls. This prominent discovery corroborated the existence of the free radicals and made a name for Paneth. Later, Calingaert¹²²⁸ (1925), Taylor and Jones¹²²⁹ (1930), Simons, McNamee, and Hurd¹²³⁰ (1932), Meinert¹²³¹ (1933), Cramer¹²³² (1934) and Garzuly¹²³³ (1935) studied the thermal decomposition of tetraalkylplumbanes. Taylor and Jones¹²²⁹ found that the thermal decomposition of Et_4Pb at $250\text{--}300^\circ\text{C}$ led to metallic lead and a mixture of gaseous and liquid hydrocarbons ($\text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{C}_4\text{H}_8, \text{C}_6\text{H}_{12}$), formed by the ethyl radicals generated in this process. According to Calingaert¹²²⁸,

the thermolysis of tetraethylplumbane over pumice gave a mixture of butane (40%), ethane and ethylene. Simons, McNamee and Hurd¹²³⁰ identified the gaseous hydrocarbons $\text{HC}\equiv\text{CH}$, $\text{CH}_2=\text{CH}_2$, $\text{MeCH}=\text{CH}_2$, $\text{Me}_2\text{C}=\text{CH}_2$, CH_4 , C_2H_6 , and small amounts of liquid hydrocarbons as well as H_2 among the products of Me_4Pb thermolysis. Razuvaev, Vyazankin and Vyshinskii¹²³⁴ (1959) showed that the thermal decomposition of Et_4Pb was a multiple chain process involving the consequent cleavage of $\text{Et}_3\text{Pb}^\bullet$ and the intermediate formation of $\text{Et}_3\text{PbPbEt}_3$ and Et_2Pb which terminated with lead precipitation. A year later these authors studied the kinetics of the thermolysis of Et_4Pb and its mixtures with $\text{Et}_3\text{PbPbEt}_3$ ¹²⁰³. The catalytic effect of the formed metallic lead on this process was also established. The investigations of Razuvaev and coworkers demonstrated for the first time that during the homolytic cleavage of the C—Pb bonds in R_4Pb an intermediate formation of a Pb—Pb bond took place. The easy decomposition of the intermediates R_3PbPbR_3 and R_2Pb resulted finally in metallic lead. As a consequence of the homolytic C—Pb and Pb—Pb bond cleavages we deal with their reaction in this section in spite of the fact that Section IV. J is devoted to organolead compounds containing Pb—Pb bonds. The dissociation of tetraalkylplumbanes into free radicals was carried out photochemically under UV irradiation. In 1936, Leighton and Mortensen¹²³⁵ showed that the photolysis of gaseous Me_4Pb resulted in lead and ethane. Photolytic decomposition of Ph_4Pb in aromatic hydrocarbons was investigated in McDonald's¹²³⁶ (1959) and Razuvaev's¹²³⁷ (1963) laboratories. The formation of metallic lead and biphenyl in benzene solution¹²³⁷ as well as the formation of 2- or 3-isopropylbiphenyl in cumene medium¹²³⁶ was observed. The use of a ^{14}C -labelled benzene and cumene solvents showed that, on photolysis of Ph_4Pb , the formed phenyl radicals reacted with the solvent. Hexaphenyldiplumbane $\text{Ph}_3\text{PbPbPh}_3$ was apparently the intermediate decomposition product. It confirmed that Pb-centered free radicals $\text{R}_3\text{Pb}^\bullet$ were the first products of the R_4Pb thermolysis.

In 1918, Grüttner¹¹¹⁸ was the first who called attention to the thermal decomposition of organylhaloplumbanes and found that Ph_3PbBr was decomposed to give PbBr_2 even at its melting point (166°C). In 1925, Calingaert¹¹⁴⁵ started to investigate in detail the thermolysis of organylhaloplumbanes. He found that during thermal decomposition of Et_3PbX ($\text{X} = \text{Cl}, \text{Br}$), Et_4Pb and Et_2PbX_2 were formed. This observation initiated a study of the thermal disproportionation (dismutation) reactions of organylhaloplumbanes. Twenty-three years later Calingaert and coworkers¹¹⁴⁸ found that Et_3PbBr was spontaneously decomposed at room temperature with formation of Et_2PbBr_2 within 50 hours. In 1932, Austin¹¹³⁶ showed that Ph_3PbCl was transformed to Ph_4Pb and Ph_2PbCl_2 in boiling butanol. The products of the disproportionation reaction of Et_3PbCl were Et_4Pb and PbCl_2 . In 1938, Evans¹²³⁸ pointed out that Bu_4PbCl , PbCl_2 and BuCl were the products of the thermal decomposition of Bu_2PbCl_2 . In 1939, Gilman and Apperson¹²³⁹ found that the thermolysis of Et_2PbCl_2 behaved analogously. In 1948, Calingaert and coworkers¹¹⁴⁸ studied the hydrothermal decomposition of Et_3PbX and Et_2PbX_2 ($\text{X} = \text{Cl}, \text{Br}$) during steam distillation: Et_3PbX was transformed to Et_2PbX_2 and Et_4Pb and Et_2PbX_2 to Et_3PbX , PbX_2 and C_4H_{10} , respectively. The authors assumed that the extremely unstable EtPbX_3 was the intermediate product of this reaction. As a summary: the decomposition products of Et_3PbX and Et_2PbX_2 were identical, but their ratios were different. Hydrothermal decomposition of Et_2PbBr_2 occurred instantly, and for Et_2PbCl_2 it happened over a period of two minutes. In contrast, Et_3PbX rather slowly decomposed by steam, but Et_3PbBr decomposed faster than Et_3PbCl . The thermolysis of Et_3PbOH and $\text{Et}_2\text{Pb}(\text{OH})_2$ ^{1148, 1239, 1240} and organylacyloxyplumbanes $\text{R}_{4-n}\text{Pb}(\text{OCOR}')_n$ ¹²⁴¹ was also studied in 1939–1962 (see Section IV.F).

The hydrogenolysis of the C—Pb bond in R_4Pb ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$) was first studied in the Ipatiev^{741–743, 1220–1224} laboratory. Since 1929, his coworkers Razuvaev and

Bogdanov^{1220–1222} as well as Koton^{1222,1224} illustrated that Ph_4Pb was decomposed under a pressure of 60 atm hydrogen at 175–225 °C to metallic lead and benzene. Tetraalkylplumbanes R_4Pb ($\text{R} = \text{Me}, \text{Et}$) under such conditions precipitated a metallic lead even at 125 °C and 100 °C, respectively^{1220,1221}. In 1930–1932, Adkins and coworkers^{1242–1245} followed the Russian scientists in studying the hydrogenation of tetraorganylplumbanes. They found that R_4Pb ($\text{R} = \text{Alk}$) was cleaved by hydrogen with formation of the corresponding alkanes RH and Pb^{1242} . Hydrogenolysis of tetraarylplumbanes Ar_4Pb ($\text{Ar} = \text{Ph}, 4\text{-MeC}_6\text{H}_4$) led to a quantitative formation of the corresponding diaryls and metallic lead at 200 °C under H_2 pressure of 125 atm. Tetraheptylplumbane under these conditions was transformed to tetradecane in only 62% yield. In 1931, Adkins and Covert¹²⁴³ found that Ni catalyzed the cleavage of tetraalkyl- and tetraarylplumbanes. In 1932, Zartmann and Adkins¹²⁴⁵ found that catalytically active Ni significantly decreased the thermolysis temperature of R_4Pb ($\text{R} = \text{Alk}, \text{Ar}$) to 200 °C under H_2 pressure. The hydrocarbons R-R were formed in a high yield as the recombination products of the R radicals. In the absence of Ni the precursor Ph_4Pb did not change under the experimental conditions, and under nitrogen pressure at 200 °C it did not change with or without Ni. These data contradicted the results gained by Ipatiev and his coworkers^{1220,1223}. In 1933, Razuvaev and Koton^{743,1222} studied a catalytic effect of Cu, Ag, Au, Ni and Pd on the destruction of Ph_4Pb by hydrogen under pressure. In the presence of these metals (except Pd) its decomposition proceeded at low temperatures and led to Pb and C_6H_6 . Palladium catalyzed only the thermal decomposition of Ph_4Pb (but not the hydrogenolysis process) to form biphenyl, but not benzene. It cannot be believed that Ipatiev remembered in the twilight of his life the investigations on hydrogenolysis of metalloorganic compounds carried out during his Soviet period. In the article of Gershbein and Ipatiev⁷⁴⁴ published already after Ipatiev's death, the hydrogenolysis results of Ph_4M ($\text{M} = \text{Pb}, \text{Sn}$) obtained at the Ipatiev laboratory in the USSR were confirmed without using new experiments. It was reported that, at 200 °C and under an initial H_2 pressure of 60 atm, Ph_4Pb was decomposed to Pb, C_6H_6 and a trace amount of Ph_2 (i.e. nothing new). The composition of the products remained unchanged when copper powder was added to the reaction (as was known earlier). The appearance of this article was unfortunate.

The heterolytic cleavage of the C–Pb bond was especially easy in a series of organometallic compounds of the silicon subgroup. In 1887, Polis¹²⁴⁶ was the first to find C–Pb bond cleavage in tetraalkylplumbanes with halogens. He demonstrated that by bubbling chlorine through a CS_2 solution of Ph_4Pb , the Ph_2PbCl_2 was the product formed. Similarly, Ph_4Pb with bromine in CS_2 or in CHCl_3 media was transformed to Ph_2PbBr_2 . A year later Polis¹²⁴⁷ synthesized $(4\text{-MeC}_6\text{H}_4)_2\text{PbX}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) by the action of chlorine, bromine and iodine on $(4\text{-MeC}_6\text{H}_4)_4\text{Pb}$. In 1904, Pfeiffer and Trüskier¹¹⁶⁵ prepared Et_3PbCl by chlorination of Et_4Pb with strong cooling. Following him in 1916, Grüttner and Krause¹¹¹⁰ showed that halogens cleaved only one of the R–Pb bonds in tetraalkylplumbanes with formation of R_3PbX only at low temperatures (–70 °C). The reaction of gaseous chlorine with R_4Pb ($\text{R} = \text{Me}, \text{Et}$) at –70 °C in ethyl acetate solution led to R_3PbCl in a quantitative yield. The chlorination of Me_3PbCl at –10 °C also resulted in a quantitative formation of Me_2PbCl_2 . Later, R_3PbX or R_2PbX_2 were synthesized similarly by the reaction of chlorine or bromine with R_4Pb ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, i\text{-Bu}, i\text{-Am}, c\text{-C}_6\text{H}_{11}$) at an appropriate temperature^{1108,1110,1114,1188}. In 1921, Grüttner and Krause¹¹⁰⁸ succeeded in synthesizing $(c\text{-C}_6\text{H}_{11})_3\text{PbI}$ and $(c\text{-C}_6\text{H}_{11})_2\text{PbI}_2$ by cleavage of $(c\text{-C}_6\text{H}_{11})_4\text{Pb}$ with iodine. Only in 1938, by the reaction of iodine with Me_4Pb in ether at 60 °C, did Calingaert and Soroos¹¹⁸⁸ prepare Me_3PbI in 60% yield. The realization of the reaction of iodine with Et_4Pb at –65 °C allowed Juenge and Cook¹¹⁷⁷ (1959) to synthesize Et_3PbI (in 73% yield). The reaction of halogens with Ar_4Pb even at

-75°C resulted in cleavage of two aryl groups with the formation of Ar_2PbX_2 . Gerchard and Gertruda Grüttner¹¹¹⁹ succeeded in obtaining Ar_3PbBr by the reaction of bromine in pyridine solution with Ar_4Pb at -15°C , i.e. with the $\text{Py} \cdot \text{Br}_2$ complex. In 1939, Gilman and Bailie¹¹⁷⁰ used this method to synthesize $(3\text{-MeC}_6\text{H}_4)_3\text{PbBr}$. They also obtained 88% of Ph_3PbI by the reaction of iodine with Ph_4Pb in CHCl_3 at room temperature. Investigations of Grüttner and Krause¹¹¹⁴ (1917) and later Calingaert and Soroos¹¹⁸⁸ (1938) demonstrated that, during the action of halogens on mixed tetraalkylplumbanes, the smaller alkyl group could be eliminated more easily. A phenyl group^{1115,1124} still cleaved easily from a Pb atom and a cyclohexyl group¹¹²¹ was eliminated with more difficulty. When Me_3PbEt was brominated at -70°C , Me_2EtPbBr was formed, and at -10°C , MeEtPbBr_2 was the product. By the reaction of bromine with *i*-Am(Pr)PbMe₂, *i*-Am(Pr)MePbBr (the latter compound with an assymetric lead atom) and AmPrPbBr₂ were subsequently obtained.

A series of organolead dihalides $\text{RR}'\text{PbX}_2$ ($\text{R} = \text{Et, Pr, Bu}$; $\text{R}' = \text{Bu, } i\text{-Bu, } i\text{-Am}$; $\text{X} = \text{Cl, Br}$)^{1114,1128} was prepared by the detachment of the low alkyl radicals from mixed tetraalkylplumbanes with bromine or chlorine. Juenge and Cook¹¹⁷⁷ prepared $(\text{CH}_2=\text{CH})_2\text{PbCl}_2$ by chlorination of $(\text{CH}_2=\text{CH})_4\text{Pb}$ in acetic acid solution at room temperature in 1959. It was remarkable that chlorine cleaved the C—Pb bond more easily than it was added to the double bond. In 1921, Krause¹¹²¹ demonstrated that $(c\text{-C}_6\text{H}_{11})_{4-n}\text{PbX}_n$ ($\text{X} = \text{Br, I}$; $n = 1, 2$) was obtained preferably by the $(c\text{-C}_6\text{H}_{11})_3\text{PbPb}(\text{C}_6\text{H}_{11}\text{-}c)_3$ cleavage with bromine or iodine. In 1917, Grüttner and Krause¹¹¹⁴ found that cleavage of $(i\text{-Bu})_3\text{PbCl}$ by bromine gave $(i\text{-Bu})_2\text{PbClBr}$ and *i*-BuBr. When Flood and Horvitz⁸⁵⁶ (1933) studied the cleavage of R_3MX ($\text{M} = \text{Si, Ge, Sn, Pb}$; $\text{X} = \text{Hal}$) with halogens, they found that Ph_3PbX ($\text{X} = \text{Cl, I}$) reacted with iodine in CCl_4 to form PhI , Ph_2PbClI and Ph_2PbI_2 , respectively.

The ability of the C—Pb bond to be cleaved with proton acids was shown in the 19th century. In 1859, Buckton⁶⁰⁴ was the first to introduce the cleavage reaction of alkyl radical from the Pb atom by the action of gaseous HCl on Et_4Pb with the formation of Et_3PbCl . Others^{1165,1248} followed the procedure. Cahours⁵⁹⁶ (1862) and Pfeiffer and Trüskier¹¹⁶⁵ (1904) repeated the reaction. Pfeiffer and coworkers^{1166,1249} obtained organylhaloplumbanes by bubbling dry HCl or HBr through an ethereal R_4Pb solution.

Browne and Reid¹²⁵⁰ (1927), Gilman and Robinson¹²⁵¹ (1930) and Catlin¹²⁵² (1935) found that the reaction of saturated HCl solution with Et_4Pb led to Et_3PbCl . Gilman and Robinson¹²⁵¹ showed that the reaction of HCl with Et_4Pb could lead to Et_3PbCl and Et_2PbCl_2 , depending on the reaction conditions. In 1939, Gilman and Bailie¹¹⁷⁰ obtained Et_3PbBr when gaseous HBr reacted with Et_4Pb . Austin¹²⁵³ (1931), Gilman and coworkers^{1170,1184,1254} (1939, 1950), Bähr¹²⁵⁵ (1947) and Juenge and Cook¹¹⁷⁷ (1959) also described the Ar_4Pb cleavage by HCl. Möller and Pfeiffer¹¹⁶⁶ (1916), Hurd and Austin^{1180,1256} (1931, 1933), Gilman and coworkers¹²⁵⁷ (1933), Calingaert, Soroos and Shapiro¹²⁵⁸ (1940), Stuckwisch¹²⁵⁹ (1943), Calingaert and coworkers¹²⁶⁰ (1945), Heap and coworkers¹²⁴¹ (1951) and Koton and coworkers¹²⁶¹ (1960) studied the relative order of elimination of organic substituents from the lead atom in mixed tetraorganylplumbanes. In 1931, Austin¹²⁶² showed that the reaction of gaseous HCl with PhPbEt_3 led to Et_3PbCl and C_6H_6 . Two year later¹¹⁸⁰ he found that the more electronegative group (according to the 'Kharasch row'¹²⁶³) was the first to cleave when HCl acted on mixed tetraarylplumbanes. Thus, for example^{1264,1265}, Ph_3PbCl ¹¹⁸⁰ was formed from $4\text{-MeC}_6\text{H}_4\text{PbPh}_3$, PrPh_2PbCl from PrPbPh_3 and $\text{PrPh}(2\text{-MeC}_6\text{H}_4)\text{PbCl}$ ¹¹⁸⁰ from $\text{Pr}(2\text{-MeC}_6\text{H}_4)_2\text{PbPh}$. According to Gilman and coworkers^{1264,1265} (1932, 1936) and other investigators mentioned above, the ease of eliminating the substituents from lead

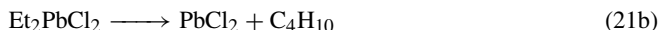
atom decreased in the following order: 2-Thi > 2-Fu > 1-C₁₀H₇ > All > CH=CHPh. Alkyl groups, as well as CH₂Ph, CH₂CH₂CH=CH₂ and 4-MeOC₆H₄ were bonded more strongly to the lead atom than Ph^{1254,1257}. Delhaye and coworkers¹²⁶⁶ found a second order kinetics for the cleavage of Me₃PbPh with HCl in methanol. In 1935, Yakubovich and Petrov¹²⁶⁷ obtained both Et₃PbCl and Et₂PbCl₂ by the reaction of gaseous HCl with Et₄Pb. In the second quarter of the 20th century (1945) numerous methods for the preparation of organolead compounds were used in the Calingaert laboratory¹²⁶⁰. It was found that R₃PbBr and R₂PbCl₂ prepared by the reaction of R₄Pb (R = Alk) with HBr and HCl in ether were contaminated with PbBr₂ and PbCl₂. However, pure R₃PbCl was obtained in a high yield by bubbling HCl through a 5–10% solution of R₄Pb in hexane. This method surpassed the methods described previously for the preparation of R₃PbCl, which used concentrated hydrochloric acid^{596,1250}. In 1945, Calingaert and coworkers¹²⁶⁰ prepared Me₃PbCl when cleaving Me₄Pb with hydrogen chloride. Later, R₃PbCl with R = Pr, *i*-Bu, CH₂=CH^{1149,1150,1177} and Pr₂PbCl₂¹¹⁵⁰ were prepared analogously. In 1951, Saunders and coworkers¹²⁴¹ prepared Et₂PbCl₂ in 80% yield when bubbling dry HCl through an Et₄Pb solution in toluene at 90 °C. Under long-time boiling, all ethyl groups were cleaved off to give PbCl₂. Earlier, in 1949, they considered the reaction of R₄Pb with saturated HCl in ether solution to be the best method for the synthesis of trialkylchloroplumbanes¹¹⁴⁹.

In 1887–1888, Polis^{1246,1247} showed that the C–Pb bonds in Ar₄Pb (Ar = Ph, 4-MeC₆H₄) were cleaved by inorganic and organic acids (HNO₃, HCOOH, MeCOOH) with the formation of appropriate salts Ar₂PbX₂ (X = NO₃, OOH, OOCMe). In the following century the reaction of tetraarylpbumbane with organic acids was carried out (see Section IV.F) by Goddard and coworkers⁷²⁸ (1922), Gilman and Robinson¹²⁵¹ (1930) and Koton^{1268,1269} (1939, 1941). In 1916, Möller and Pfeiffer¹¹⁶⁶ found that aryl groups were cleaved off more easily than alkyls from lead atom of Ph₂PbEt₂ with inorganic acids. In 1925, Krause and Schlöttig¹¹²⁴ reached the same conclusion when they cleaved Ph₂PbR₂ (R = Me, Et, *c*-C₆H₁₁), while Calingaert¹¹⁴⁵ (1925) and Hurd and Austin¹²⁵⁶ (1931) concluded likewise when conducting the cleavage of PhPbEt₃. In 1931–1932, Austin^{680,1262} demonstrated that the (2-MeC₆H₄)–Pb and (4-MeC₆H₄)–Pb bonds cleaved more easily than the Ph–Pb bond. According to Austin¹²⁶² (1931) and McCleary and Degering¹²⁷⁰ (1938), two ethyl groups are usually cleaved off from Et₄Pb in the reaction with nitric acid with the formation of Et₂Pb(NO₃)₂. The reaction of Et₄Pb with H₂SO₄ proceeds in the same way. Jones and coworkers¹²⁷¹ carried out the reaction of HNO₃, H₂SO₄ and HCl with R₄Pb (R = Pr, Bu, Am) which led to R₂PbX₂.

In 1930, Gilman and Robinson¹²⁴⁸ showed that HSO₃Ph cleaved Et₄Pb to form Et₃PbSO₃Ph. Gilman and Robinson (1929) obtained selectively Ph₃PbCl or Ph₂PbCl₂¹²⁷² by the reaction of gaseous HCl with Ph₄Pb.

Remarkably, according to Krause and Schlöttig¹¹²⁴ (1925) even NH₄Cl cleaved at 170–180 °C the C–Pb bond of Et₄Pb with formation of Et₃PbCl. Analogously, in 1948, Koton¹²⁷³ prepared Ph₃PbCl by heating a mixture of Ph₄Pb and Me₃N·HCl at 130 °C. In the early part of the last century it was established that tetraorganylplumbanes R₄Pb (R = Alk, Ar) cleaved by some metal and nonmetal halides with the formation of R₃PbX and R₂PbX₂. So triethylchloroplumbane, as well as the products of ethylation of the corresponding element chlorides were formed during the reaction of Et₄Pb with HgCl₂^{774,1274,1275}, AlCl₃^{817,1239,1276}, SiCl₄^{1250,1277}, TiCl₄¹²⁷⁸, PCl₅, BiCl₃⁸¹⁹ and FeCl₃¹²³⁹ and also RCOCl (R = Me, Ph)¹²⁵⁰. In particular, Gilman and Apperson¹²³⁹ found in 1939 that the first reaction product of Et₄Pb with AlCl₃ was Et₂PbCl₂. The further process could be described by equations 21a and 21b.

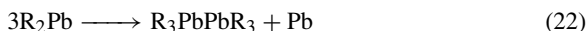




In 1934 Kocheshkov and Nesmeyanov^{813,1279} and in 1949 Hein and Schneider¹²⁸⁰ carried out the dearylation reaction of Ph_4Pb by mercury dihalides, which led to Ph_3PbX and Ph_2PbX_2 ($\text{X} = \text{Cl}, \text{Br}$). According to Panov and Kocheshkov^{1281–1283} (1952, 1955) $\text{Hg}(\text{OOCR})_2$ smoothly cleaved off phenyl groups from Ph_4Pb in the corresponding carboxylic acid medium to consequently form $\text{Ph}_{4-n}\text{Pb}(\text{OCOR})_n$ with $n = 1–4$. In the case of tetraalkylplumbane $\text{R}'_4\text{Pb}$ ($\text{R}' = \text{Alk}$) such reaction resulted in $\text{R}'_2\text{Pb}(\text{OCOR})_2$ formation. In 1949–1959 the possible dearylation process of Ph_4Pb with TlCl_3 ¹²⁷⁸, PCl_3 ^{1284–1286}, AsCl_3 ^{1284,1285}, SbCl_3 and SbCl_5 ¹²⁸⁵ was shown to result in the formation of Ph_2PbCl_2 and Ph_2TlCl , Ph_2PCl , Ph_2AsCl , Ph_2SbCl and Ph_2SbCl_3 , respectively. The results mentioned above showed that tetraorganylplumbanes could be used as specific alkylating and arylating agents. In 1919, Krause and Schmitz⁸¹⁴ showed the possibility of C–Pb bond cleavage by silver nitrate in the case of Ph_4Pb . The reaction products were $\text{Ph}_2\text{Pb}(\text{NO}_3)_2$ and metastable PhAg , which easily decomposed to Ph_2 and Ag . The R_4Pb ($\text{R} = \text{Alk}, \text{Ar}$) cleavage by silver nitrate was further used by many investigators⁵⁴, as shown by the 13 publications devoted to the reaction.

The coproportionation reaction ('*komproportionierung*'), which was so well developed in organotin chemistry, did not attract attention in organolead chemistry for a long time. This was because PbCl_4 , which should be used in this reaction, was both unstable and has a chlorination action. In 1932, Austin¹¹³⁶ showed that the interaction of Ph_4Pb and Ph_2PbCl_2 led to Ph_3PbX . In 1968, Willemsens and van der Kerk¹²⁸⁷ replaced PbCl_4 with the more stable $\text{Pb}(\text{OOCMe})_4$ in the presence of catalytic amounts of mercury diacetate (Section IV.F). The processes of radical rearrangement in a mixture of two tetraorganylplumbanes (which could be attributed to coproportionation) in the presence of Lewis acids (such as BF_3 , AlCl_3 , SnCl_4 , EtPbX) as catalysts were studied in detail by Calingaert and coworkers^{1276,1288–1291}. When carried out at relatively low temperatures^{1276,1288–1291} these processes led to a mixture of tetraorganylplumbanes including all possible combinations of substituents present in the starting reagents. However, isomerization of alkyl groups was not observed. For example, during the coproportionation of an equimolecular mixture of Me_4Pb and Et_4Pb (mol%): Me_3PbEt (25%), Et_3PbMe (25%) and Me_2PbEt_2 (37.5%) were formed together with only about 6.25% of the unreacted precursors Me_4Pb and Et_4Pb . Calingaert and coworkers^{1258,1260} (1940–1945) called attention to the dealkylation reaction of nonsymmetric tetraalkylplumbanes with HCl , which was often accompanied by disproportionation of the formed trialkylchloroplumbanes that led to several reaction products.

Further disproportionation reaction is important in organolead chemistry. As reported in Section III. C, tetraorganylplumbanes were obtained by reacting PbCl_2 with organometallic compounds via the intermediates :PbR_2 . The processes were accompanied by cleavage and formation of C–Pb and Pb–Pb bonds as described by equations 22 and 23.



The results of these reactions depended essentially on the nature of the substituent (mainly on steric factors). The first reaction of aliphatic organometallic compounds with PbCl_2 was so fast that it was impossible to stop it at the stage of R_2Pb formation. However, $\text{Ar}_2\text{PbAr} = \text{Ph}, 4\text{-MeC}_6\text{H}_4$ was proved to be rather stable and it was possible to synthesize it by the organomagnesium method at a low temperature. Even at 20°C the reaction resulted in $\text{Ar}_3\text{PbPbAr}_3$, and at the temperature of boiling ether it led to Ar_4Pb . It might be emphasized that these reactions depended considerably on the

nature of the substituent at the lead atom. The studies of Krause and Reissaus^{1122,1292} (1921, 1922), Austin¹²⁶² (1931), Calingaert and Soroos¹¹⁸⁸ (1938) and Gilman and Bailie¹¹⁷⁰ (1939) clearly demonstrated that the steric factor in the disproportionation reaction of R_3PbPbR_3 played a very essential role. When $R = Ph$ and $4-MeC_6H_4$ the reaction led easily to R_4Pb ^{1122,1170,1292}. If $R = 2-MeC_6H_4$ the disproportionation became difficult^{1122,1170,1262,1292} and when $R = 2,4,6-Me_3C_6H_2$, $2,4-Me_2C_6H_3$ and $c-C_6H_{11}$ the process did not proceed. According to Calingaert and Soroos¹¹⁸⁸ and Gilman and Bailie¹¹⁷⁰ the tendency to disproportionate increased in the following order: $2,4,6-Me_3C_6H_2 < c-C_6H_{11} < 1-C_{10}H_7 < 2-ROC_6H_4 < 2-MeC_6H_4 < 4-ROC_6H_4 < 4-MeC_6H_4 < 3-MeC_6H_4 < Ph < Et < Me$. Calingaert¹¹⁴⁵ (1925) was the first to observe the disproportionation of alkylchloroplumbanes. Later, together with coworkers he found that a mixture of $Me_{4-n}PbEt_n$ ($n = 0-4$) as well as of $MeEt_2PbCl$ and Et_3PbCl ¹²⁵⁸ was formed by boiling $EtMe_2PbCl$. In 1932, Austin¹¹³⁶ reported the transformation of Ph_3PbCl into Ph_4Pb and Ph_2PbCl_2 . In 1960, Razuvaev and coworkers¹²⁹³ found out that thermal decomposition of Et_3PbBr at $70^\circ C$ led to Et_4Pb and Et_2PbBr_2 . Reducing agents^{1161,1294} promoted the disproportionation of organylhaloplumbanes, and Gilman and Barnett¹²⁹⁴ showed that Ph_3PbCl was transformed into Ph_4Pb in 70% yield in the presence of hydrazine¹²⁹⁴. In analogous conditions Ph_4Pb was also obtained from Ph_2PbCl_2 . In 1942, Nad' and Kocheshkov¹¹⁶¹ observed the transformation of Ar_2PbCl_2 ($Ar = Ph, 2-MeC_6H_4$) into Ar_3PbCl in the presence of metallic lead powder or its alloys with Na. In 1959–1961 investigations, carried out in the Razuvaev^{1202,1293,1295–1297} laboratory, showed that the disproportionation reactions of organolead compounds should be divided into thermal and catalytic reactions. It was established that $Et_3PbPbEt_3$, which was usually stable in the absence of air at room temperature, was easily disproportionated with the formation of Et_4Pb and Pb ^{1293,1295,1296} in the presence of a catalytic amount of HgX_2 , $EtHgX$ ($X = Cl, Br$), AlX_3 ($X = Cl, Br$), Et_3SnCl , Et_3PbBr ¹²⁹⁶ or Et_2PbBr_2 and $BrCH_2CH_2Br$ ¹²⁹³. All these catalytic reactions were not accompanied by evolution of gaseous products. According to the patent literature, silica or activated carbon^{1298,1299} could be used for the catalytic disproportionation. Free Et^\bullet radicals stimulated the formation of gaseous products and were generated along with the formation of Et_4Pb and Pb in the thermal disproportionation of $Et_3PbPbEt_3$. The intermediate product of this process was $PbEt_2$ ^{1202,1203,1297,1300}.

Thermal disproportionation of Et_3PbOH at $150^\circ C$ and its kinetics were studied by Alexandrov and coworkers in 1959¹²⁴⁰. The thermolysis reaction products were Et_4Pb , $Et_2Pb(OH)_2$ as well as H_2O , C_2H_4 , C_2H_6 and C_4H_{10} . In 1961, Alexandrov and Makeeva¹³⁰¹ showed that $Et_2Pb(OOCMe)_2$ disproportionated into $Et_3PbOOCMe$ and $EtPb(OOCMe)_3$, but the latter immediately decomposed to $Pb(OOCMe)_2$ and $MeCOOEt$. Analogously, $Et_2Pb(OOCCl)_2$ disproportionated^{1271,1241}.

F. Compounds having a Pb—O Bond

The majority of organolead compounds having the Pb—O bond have the following formulas: $R_{4-n}Pb(OH)_n$ ($n = 1-3$), $R_3PbOPbR_3$, $(R_2PbO)_n$, $(RPbOOH)_n$, $R_{4-n}Pb(OR')_n$ ($n = 1, 2$) and $R_{4-n}Pb(OOCR')_n$ ($n = 1-3$). They were studied less intensively than their organogermanium and organotin analogs. Nevertheless, the number of known organolead compounds with a Pb—O bond reached 200 by 1953. In 1853, Löwig⁴² obtained the first representative of trialkylplumbanols Et_3PbOH by the reaction of Et_3PbI or $(Et_3Pb)_2CO_3$ with moist silver oxide or with aqueous alkali in ether medium. He showed that the compound was a typical base, which was neutralized by inorganic acids HX ($X = Cl, Br, I, NO_3, 0.5SO_4$) with the formation of the corresponding salts Et_3PbX . In 1860,

Klippel^{1217,1218}, following Löwig⁴² synthesized Et_3PbOH (which he considered to be a monohydrate of hexaethyldiplumboxane) by the reaction of Et_3PbI with moist Ag_2O , followed by water treatment. He found also that Et_3PbOH was formed in the reaction of Et_3PbNO_3 with alcoholic KOH solution. However, Klippel^{1217,1218} found this method less convenient. He synthesized a series of triethylacyloxyplumbanes Et_3PbOOCR ($\text{R} = \text{H}, \text{Me}, \text{Pr}, \text{Ph}$) as well as triethylplumbyl derivatives of oxalic, tartaric, hydrocyanic and cyanic acids by the neutralization of Et_3PbOH with the corresponding acids. In the 19th century Buckton⁶⁰⁴ (1859) and Cahours⁵⁹⁶ (1862) also synthesized trialkylplumbanols. In the 20th century Pfeiffer and Trüskier¹²⁴⁹ (1916), Krause and Pohland¹¹²³ (1922), Calingaert and coworkers¹¹⁴⁰ (1923), Browne and Reid¹²⁵⁰ (1927), Bähr¹²⁵⁵ (1947) and Saunders and Stacey¹¹⁵⁰ (1949) used the methods mentioned above for the synthesis of R_3PbOH . Calingaert and coworkers¹²⁶⁰ (1945) found that the reaction of Et_3PbX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with aqueous alkali in ether did not lead to pure Et_3PbOH due to contamination by the starting Et_3PbX . They showed that pure Et_3PbOH could be obtained by modification of two methods described earlier. The ether was replaced by benzene during the alkaline hydrolysis of Et_3PbX , and an aqueous solution of Et_3PbCl was used during the Ag_2O hydrolysis. The yield of triethylplumbanol then reached 93%. It was also established that the reaction of an aqueous solution of Et_3PbOH with CO_2 led to $(\text{Et}_3\text{Pb})_2\text{CO}_3$, and with excess of CO_2 to $\text{Et}_3\text{Pb}(\text{HCO}_3)$, a compound which was previously unknown. A hydrolytic method for the synthesis of Ar_3PbOH (mainly Ph_3PbOH) from Ar_3PbX was described by Grüttner¹¹¹⁸ (1918) and Krause and Pohland^{1123,1302} (1922, 1938). In 1921, Krause¹¹²¹ obtained the first tricyclohexylplumbanol by the reaction of $(\text{c-C}_6\text{H}_{11})_3\text{PbI}$ with 30% KOH.

Another method for the preparation of R_3PbOH was based on the oxidation of R_3PbPbR_3 by potassium permanganate in acetone. Austin¹²⁶² (1931) and Bähr¹²⁵⁵ (1947) obtained Ar_3PbOH ($\text{Ar} = \text{Ph}, 2,4\text{-Me}_2\text{C}_6\text{H}_3$) in the same way. In 1959, Razuvaev and coworkers¹³⁰³ isolated Et_3PbOH when $\text{Et}_3\text{PbPbEt}_3$ was oxidized by organic peroxides.

Jones and coworkers¹²⁷¹ (1935), Schmidt¹³⁰⁴ (1938), Calingaert and coworkers^{1148,1260} (1945, 1948), Saunders and coworkers¹²⁴¹ (1951) and Alexandrov and coworkers¹²⁴⁰ (1959) synthesized diorganylplumbanediols $\text{R}_2\text{Pb}(\text{OH})_2$ ($\text{R} = \text{Alk}, \text{Ar}$). In 1935 and 1940, Lesbre^{1176,1305} reported the synthesis of organylplumbanetriols by the reaction of alkyl iodides with an alkaline solution of lead oxide (i.e. $\text{NaPb}(\text{OH})_3$) at 5°C . These compounds were regarded as hydrated alkylplumbane acids.

Trialkylplumbanols as well as triorganylstannanols have no tendency to undergo the reaction of anhydrocondensation and that is their main difference from R_3MOH with $\text{M} = \text{Si}, \text{Ge}$. Only in 1960–1962 did Brilkina and coworkers^{1306,1307} succeed in transforming R_3PbOH to $\text{R}_3\text{PbOPbR}_3$ by the action of metallic sodium, which did not form R_3PbONa . Up to 1964¹⁰⁹ only three hexaorganyldiplumboxanes $\text{R}_3\text{PbOPbR}_3$ with $\text{R} = \text{Et}$ ^{43,1217,1218,1306–1311}, *i*-Am^{1217,1218} and Ph^{1118,1254,1256,1306} appeared in the literature. Löwig⁴³ (1853) reported the first representative of hexaalkyldiplumboxanes $\text{Et}_3\text{PbOPbEt}_3$, which was obtained by alkaline hydrolysis of Et_3PbI . In 1860, Klippel^{1217,1218} synthesized $\text{R}_3\text{PbOPbR}_3$ with $\text{R} = \text{i-Am}$ by the reaction of *i*-Am₃PbI with moist silver oxide, followed by water treatment.

Et_3PbOH (*'methplumbäthoxyhydrat'*) was obtained analogously from Et_3PbI . The reaction of the latter with CO_2 led to $(\text{Et}_3\text{Pb})_2\text{CO}_3$. Although Löwig⁴³ and other authors reported that they had obtained $\text{Et}_3\text{PbOPbEt}_3$ by different methods involving water or even air moisture, it could not be true because this compound is extremely unstable hydrolytically. Apparently they dealt with Et_3PbOH . In 1918, Grüttner¹¹¹⁸ mentioned for the first time hexaphenyldiplumboxane $\text{Ph}_3\text{PbOPbPh}_3$. He assumed that it was obtained by the reaction of Ph_3PbBr with hot alcoholic KOH or NaOH solution, followed by

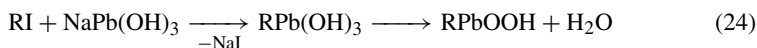
treatment with water or by shaking of Ph_3PbBr with 10% aqueous alkali in the cold. Actually, it was Ph_3PbOH . Up to 1960 hexaorganyldiplumbioxanes were neither isolated nor characterized. The compounds with $\text{R} = \text{Et}, \text{Ph}$ were hardly formed because their syntheses were conducted in aqueous or water–alcohol media, in which they were very easily hydrolyzed with the formation of R_3PbOH . Austin^{1253,1262} (1931) and Bähr¹²⁵⁵ (1947) assumed that the labile $\text{Ph}_3\text{PbOPbPh}_3$, the isolation and characterization of which had failed, was apparently the intermediate in the oxidation reaction of $\text{Ph}_3\text{PbPbPh}_3$ which led to Ph_3PbOH . At the beginning of the 1960s Russian chemists^{1306,1307} developed the most convenient preparative method of hexaorganyldiplumbioxane. It was based on the reaction of triorganyldiplumbanols with dispersed Na in benzene. Compounds $\text{R}_3\text{PbOPbR}_3$ with $\text{R} = \text{Et}$ ^{1307,1309,1310} and Ph ¹³⁰⁶ were obtained by this method and characterized.

In 1856, Klippel^{1217,1218} obtained and then published in 1860 the data which indicated the ease of $\text{Pb}—\text{O}—\text{Pb}$ group protolysis by water and acids. Particularly, he showed that during the synthesis of $\text{Et}_3\text{PbOPbEt}_3$ its monohydrate, i.e. Et_3PbOH , was formed upon contact with water. He also cleaved $\text{R}_3\text{PbOPbR}_3$ with $\text{R} = i\text{-Am}$ by hydrochloric and sulfuric acids. In 1960–1961, Alexandrov and coworkers^{1307,1309} showed that $\text{R}_3\text{PbOPbR}_3$ with $\text{R} = \text{Et}, \text{Ph}$ was easily protolyzed not only by water with formation of R_3PbOH (especially in aqueous methanol or dioxane), but also by alcohols already at -10°C . By the way, Et_3PbOH (in 95–100% yield) and Et_3PbOR ¹³⁰⁹ ($\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{Ph}, \text{CMe}_2\text{Ph}$) were formed from $\text{Et}_3\text{PbOPbEt}_3$. Analogously, $\text{Et}_3\text{PbOPbEt}_3$ was cleaved by organic hydroperoxides ROOH with the formation of Et_3PbOH in 95–100% yield and Et_3PbOOR ($\text{R} = \text{Me}_3\text{C}, \text{Me}_2\text{PhC}$). Hexaethyldiplumbioxane decomposed with formation of Et_4Pb , $(\text{Et}_2\text{PbO})_n$, ethylene and ethane¹³⁰⁹ even at $70\text{--}90^\circ\text{C}$. Hexaphenyldiplumbioxane disproportionated with the formation of Ph_4Pb and $(\text{Ph}_2\text{PbO})_n$ in xylene at 100°C ¹³⁰⁶.

The first dialkylplumbanediols $\text{R}_2\text{Pb}(\text{OH})_2$ were synthesized only in the middle of the 20th century. All were synthesized from R_2PbX_2 by alkaline hydrolysis or by the reaction with moist silver oxide^{1148,1240,1241,1260,1271,1304}. The first $\text{R}_2\text{Pb}(\text{OH})_2$ with $\text{R} = \text{Bu}, \text{Am}$ were prepared by Jones and coworkers¹²⁷¹ in 1935. Later, $\text{Et}_2\text{Pb}(\text{OH})_2$ was synthesized in the laboratory of Calingaert¹²⁶⁰ by the reaction of Et_2PbCl_2 with Ag_2O in water. $\text{Et}_2\text{Pb}(\text{OH})_2$ was isolated as hexahydrate, which transformed into polymeric $[\text{Et}_2\text{PbO}]_n$, losing water even at room temperature. It was shown that $\text{Et}_2\text{Pb}(\text{OH})_2$ was a rather weak base, like NH_4OH . Its aqueous solutions were neutralized by strong acids (HX) with the formation of the corresponding salts Et_2PbX_2 , and by saturating with CO_2 it led to Et_2PbCO_3 . Calingaert and coworkers studied the decomposition of Et_3PbOH and $\text{Et}_2\text{Pb}(\text{OH})_2$ during their contact with water steam at 100°C ¹²⁶⁰. It was found that $\text{Et}_2\text{Pb}(\text{OH})_2$ was more stable than Et_3PbOH . The initial products of the hydrothermal disproportionation of the latter were Et_4Pb and $\text{Et}_2\text{Pb}(\text{OH})_2$, which in turn decomposed into $\text{Pb}(\text{OH})_2$ and gaseous hydrocarbons. In 1951, Heap and coworkers¹²⁴¹ found also that $\text{Et}_2\text{Pb}(\text{OH})_2$ was easily dehydrated in vacuum at room temperature, and the $(\text{Et}_2\text{PbO})_n$ formed slowly decomposed with isolation of PbO at 100°C . Shushunov, Brillkina and Alexandrov¹³¹² (1959) found that high yield of $\text{Et}_2\text{Pb}(\text{OH})_2$ and insignificant yield of Et_3PbOH were formed as intermediate products during the oxidation of Et_4Pb by oxygen in nonane or in trichlorobenzene.

In 1959, Alexandrov and coworkers¹²⁴⁰ reported that $\text{Et}_2\text{Pb}(\text{OH})_2$ decomposed on heating with explosion. The thermal decomposition of both $\text{Et}_2\text{Pb}(\text{OH})_2$ and Et_3PbOH was studied in nonane medium at $40\text{--}120^\circ\text{C}$ and PbO , Et_4Pb , ethylene, ethane and butane were isolated. The intermediate decomposition product of Et_3PbOH under mild conditions was $\text{Et}_2\text{Pb}(\text{OH})_2$, and thermal decomposition of the latter led back to Et_3PbOH . In 1938, Schmidt¹³⁰⁴ reported the formation $\text{Ar}_2\text{Pb}(\text{OH})_2$. Unlike triaryldiplumbanols, these compounds were extremely unstable and easily transformed into polydiaryldiplumbioxanes $(\text{Ar}_2\text{PbO})_n$.

As early as in the 19th century the polymeric diorganylplumboxanes $(\text{Et}_2\text{PbO})_n$ were first synthesized. Already in 1853, Löwig⁴³ was the first to obtain polydialkylplumboxane $(\text{Et}_2\text{PbO})_n$ in the reaction of alkali with Et_2PbI_2 . In 1916, Grüttner and Krause¹¹¹⁰ synthesized first $(\text{Me}_2\text{PbO})_n$. In 1887, Polis¹²⁴⁶ obtained $(\text{Ph}_2\text{PbO})_n$ by the reaction of alkali with Ph_2PbI_2 . In 1927, Zechmeister and Csabay¹²¹⁹ had reproduced this synthesis. In 1955, Kocheshkov and Panov¹³¹³ demonstrated that $(\text{Ar}_2\text{PbO})_n$ with $\text{Ar} = 4\text{-MeC}_6\text{H}_4$ could be prepared by the reaction of $\text{Ar}_2\text{Pb}(\text{NO}_3)_2$ with KOH . According to them, diaryldiacyloxyplumbanes were hydrolyzed with formation of $(\text{Ar}_2\text{PbO})_n$ much more easily than the corresponding diaryldihaloplumbanes. In 1943, Hein and coworkers¹³¹⁴ obtained the first polydicyclohexylplumboxane. Polydiorganylplumboxanes did not receive the special attention of investigators and the number of publications dealing with them did not exceed 10 until 1960. The polymers, corresponding to the RPbOOH formula, i.e. the so-called organylplumbane acids, were described in more detail. Such compounds with $\text{R} = \text{Me}, \text{Et}, \text{Pr}, i\text{-Pr}, \text{Bu}, \text{CH}_2=\text{CHCH}_2$ and PhCH_2 were first obtained by Lesbre¹³⁰⁵ (1935) by the reaction of the corresponding organic iodides RI with alkaline PbO solution at 5°C ^{1176,1305} according to equation 24.



Lesbre assumed that organylplumbanetriols were intermediates of this reaction. Arylplumbane acids ArPbOOH were first obtained at the Koshechkov laboratory^{1198,1283,1313,1315} by the hydrolysis of $\text{RPb}(\text{OCOR}')_3$ with aqueous alcoholic ammonia solution. These polymeric compounds ('acids') turned out to be bases which were easily dissolved in mineral and organic acids. They could not be neutralized by aqueous Na_2CO_3 or NH_3 solution but dissolved with difficulty only in 15–20% KOH ¹³¹⁵. On long-time drying ArPbOOH converted into polyarylplumbsesquioxanes $(\text{ArPbO}_{1.5})_n$ ^{1198,1315}.

Organylacyloxyplumbanes $\text{R}_{4-n}\text{Pb}(\text{OOCR}')_n$, organolead carbonates $(\text{R}_3\text{Pb})_2\text{CO}_3$, R_2PbCO_3 and organylorganoxylplumbanes $\text{R}_{4-n}\text{Pb}(\text{OR}')_n$ are classified as organoleads containing the $\text{Pb}-\text{O}-\text{C}$ group. The latter were unknown until the second half of the last century. For the first time they appeared in Gilman and coworkers¹³⁰⁸ article. In 1962, the formation of Et_3PbOR by the reaction of $\text{Et}_3\text{PbPbEt}_3$ with ROH was reported¹³¹¹. In 1964, Rieche and Dahlmann¹³¹⁶ developed three methods for the synthesis of organolead peroxides described in equations 25–27.



The triorganyl(organylperoxy)plumbanes proved to be hydrolytically very unstable and were easily transformed into the corresponding triorganylplumbanols even under the action of air moisture. Only in 1963–1967 was a simple method for the synthesis of $\text{R}_3\text{PbOR}'$ found: by the reaction of R_3PbX ($\text{X} = \text{Cl}, \text{Br}$) with $\text{R}'\text{ONa}$ ^{1310,1311,1316–1319} under conditions which completely excluded any contact with air moisture. Trialkylalkoxyplumbanes $\text{R}_3\text{PbOR}'$ attained importance only in 1966, when Davies and Puddephatt¹³¹⁸ studied their reactions with RNCO , PhNCS , CS_2 , $\text{Cl}_3\text{CCH}=\text{O}$, $(\text{Cl}_3\text{C})_2\text{C}=\text{O}$, $\text{Cl}_3\text{CC}\equiv\text{N}$ and other compounds.

The first organylacyloxyplumbanes were synthesized in the 19th century. Klippel^{1217,1218} (1860) synthesized triethylacyloxyplumbanes Et_3PbOOCR with $\text{R} = \text{H}$,

Me, Pr, Ph by the reaction of the corresponding acids with Et_3PbOH (he thought that they were monohydrates of hexaethylplumbane) or with $(\text{Et}_3\text{Pb})_2\text{CO}_3$ (the product of Et_3PbH with CO_2). Browne and Reid¹²⁵⁰ applied this method for the synthesis of triethylacyloxyplumbane in 1927. In 1952, Panov and Kocheshkov¹²⁸¹ used the cleavage reaction of $(\text{Ar}_2\text{PbO})_n$ by carboxylic RCOOH ($\text{R} = \text{Me}, i\text{-Pr}$) acids for synthesis of $\text{Ar}_2\text{Pb}(\text{OOCR})_2$. Polis^{1246,1247} prepared in 1887 $\text{Ar}_2\text{Pb}(\text{OOCR})_2$ ($\text{Ar} = \text{Ph}, 4\text{-MeC}_6\text{H}_4$; $\text{R} = \text{H}, \text{Me}$) by heating Ar_4Pb with RCOOH . In addition, he demonstrated that diaryldiacyloxyplumbanes were involved in an exchange reaction with NH_4SCN , $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2S . In 1927, Browne and Reid¹²⁵⁰ used for the first time the cleavage reaction of Et_4Pb by eight different carboxylic acids (from acetic to pelargonic) in the presence of silica as catalyst for the synthesis of trialkylacyloxyplumbanes. Analogously, five diethyl(haloacetoxy)plumbanes $\text{Et}_2\text{PbOOCCH}_3\text{-}_n\text{X}_n$ with $\text{X} = \text{Cl}, \text{Br}$; $n = 1-3$ were synthesized. By the same method he obtained $\text{Et}_2\text{Pb}(\text{OOCMe})_2$, i.e. he showed the possibility of the cleavage of two ethyl groups from Et_4Pb by acetic acid. An attempt at synthesis of $\text{Pb}(\text{OOCMe})_4$ by the same method was unsuccessful. Browne and Reid¹²⁵⁰ also found that on heating Et_4Pb with acetic acid at over 90°C , $\text{Et}_2\text{Pb}(\text{OOCMe})_2$ was formed. Later, other experiments confirmed these data^{971,1150,1308}. For instance, on heating Et_4Pb with PhCOOH at 100°C , $\text{Et}_2\text{Pb}(\text{OOCPh})_2$ ¹²⁴¹ was prepared. In 1922, Goddard, Ashley and Evans⁷²⁸ found that on heating Ph_4Pb with aliphatic or aromatic carboxylic acids, two phenyl groups were easily eliminated with the formation of $\text{Ph}_2\text{Pb}(\text{OOCR})_2$. This method for synthesis of diaryldiacyloxyplumbanes was used later by Koton^{1268,1269} (1939, 1941) and by Panov and Kocheshkov^{1282,1283,1313} (1952, 1955). These experiments had established that the reaction rate of the acidolysis of tetraalkylplumbanes decreased as the lengths of the alkyl radicals increased.

Goddard, Ashley and Evans⁷²⁸ (1922), Gilman and Robinson¹²⁴⁸ (1930), Koton^{1268,1269} (1939, 1941) and Calingaert and coworkers¹²⁶⁰ (1945) also used this method to prepare triethylacyloxyplumbane. The latter authors¹²⁶⁰ showed that the use of silica for the $\text{Me}_3\text{PbOOCMe}$ synthesis was optional. Browne and Reid¹²⁵⁰ (1927) developed another synthesis of triethylacyloxyplumbanes based on the reaction of $\text{Et}_3\text{PbOOCMe}$ with RCOOK ($\text{R} = \text{Bu}, \text{Ph}$) in aqueous media. They carried out a similar reaction with KCN which resulted in Et_3PbCN ¹²⁵⁰. In 1930 and 1953 Gilman and Robinson^{1248,1308} used this method. Thereafter, Calingaert and coworkers¹²⁶⁰ (1945), Saunders and coworkers^{971,1149,1150,1241,1320} (1947–1951) and Gilman and coworkers¹³⁰⁸ (1953) obtained R_3PbOOCR from R_4Pb .

In 1934, Kocheshkov and Alexandrov¹³²¹ found a method for the preparation of triphenylacyloxyplumbanes based on the reaction of Ph_3PbCl with potassium salts of carboxylic acids. They first synthesized $\text{Ph}_3\text{PbOOCCH}_2\text{COOEt}$ by this method. Thermal decomposition of the latter at $160\text{--}165^\circ\text{C}$ resulted in $\text{Ph}_3\text{PbCH}_2\text{COOEt}$ and CO_2 . Analogously, $\text{Ph}_3\text{PbOOCCH}(\text{Ph})\text{COOEt}$ was obtained and its thermolysis led to $\text{Ph}_3\text{PbCH}(\text{Ph})\text{COOEt}$. Another method for the preparation of triorganylacyloxyplumbanes, based on the neutralization reaction of triorganylplumbanols by carboxylic acids, was used by Gilman and coworkers¹³⁰⁸ in 1953. They observed that sometimes the reaction of triethylplumbanol with some carboxylic acids was accompanied by cleavage of one ethyl group that led to diethyldiacyloxyplumbanes. The reaction of carboxylic acids with triarylplumbanols, developed by Koton^{1322,1323}, was of special synthetic interest.

Nad' and Kocheshkov¹¹⁶¹ first established the possibility of reacylation of organylacyloxyplumbanes by high carboxylic acids in 1942. This reaction was used at the laboratories of Kocheshkov^{1197–1199,1216,1282,1283,1315}, Nesmeyanov¹¹⁹⁵ (1948) and Saunders¹²⁴¹ (1951). In 1947, McCombie and Saunders⁹⁷¹ showed that trialkylacyloxyplumbanes could be obtained by reacylation of triethylplumbylcarbonate by carboxylic acids.

In 1953, Gilman and coworkers¹³⁰⁸ proposed an unusual method for reacylation of triethylacetoxylplumbane. They found that insoluble Et_3PbOOCR was immediately precipitated when an aqueous solution of triethylacetoxylplumbane was mixed with the sodium salts of higher carboxylic acids RCOONa .

In 1952, Panov and Kocheshkov¹²⁸¹ employed the reaction of trialkylacyloxyplumbane cleavage by mercury salts of carboxylic acids $\text{Hg}(\text{OOCR}')_2$ for the synthesis of $\text{R}_2\text{Pb}(\text{OOCR}')_2$. Triethylacetoxylplumbane was also obtained by Razuvaev and coworkers⁹⁰³ using $\text{Et}_3\text{PbPbEt}_3$ cleavage of $\text{Pb}(\text{OOCMe})_4$ in benzene media.

In 1942, Nad' and Kocheshkov¹¹⁶¹ studied in detail the reaction of $\text{Pb}(\text{OOCMe})_4$ with diarylmercury in CHCl_3 at room temperature. This appeared to be a useful method for the preparation of diaryldiacetoxylplumbane. In 1948, Nesmeyanov and coworkers^{1195,1196} used it for the synthesis of $(\text{ClCH}=\text{CH})_2\text{Pb}(\text{OOCMe})_2$.

Organolead compounds of the RPbX_3 series (R = organic substituent) were unknown up to 1952. However, in 1935–1940, Lesbre^{1176,1305,1324,1325} reported the synthesis of alkyltriiodoplumbanes RPbI_3 (but their physical constants were not given) by the reaction of alkyl iodides with CsPbCl_3 . However, Capinjala at the Calingaert laboratory¹¹⁴⁸ could not reproduce Lesbre's data. In accordance with that, Druce in 1922¹³²⁶ and Gilman and Apperson in 1939¹²³⁹ pointed out the high instability of RPbX_3 (X = halogen). The first stable representatives of organolead compounds of type RPbX_3 turned out to be arylacyloxyplumbanes $\text{ArPb}(\text{OOCR})_3$, which were obtained in a high yield by Kocheshkov, Panov and Lodochnikova^{1197–1199,1281,1283} by the reaction of $\text{Hg}(\text{OOCR})_2$ with $\text{Ar}_2\text{Pb}(\text{OOCR})_2$ ¹²⁸¹ in RCOOH media or by the reaction of Ar_2Hg with $\text{Pb}(\text{OOCR})_4$ (R = Me, Et, *i*-Pr) in CHCl_3 in 1956–1959. Aryltriacyloxyplumbanes were transformed into $\text{Ar}_2\text{Pb}(\text{OOCR})_2$ ¹¹⁹⁹ by the action of Ar_2Hg . In 1952, Panov and Kocheshkov¹²⁸¹ first prepared arylplumbane acids $(\text{ArPbOOH})_n$ by the reaction of $\text{ArPb}(\text{OOCR})_3$ with weak alkali solution or aqueous ammonia. They also carried out re-esterification of aryltriacyloxyplumbanes with carboxylic acids having higher boiling temperatures than MeCOOH (e.g. PhCOOH or $\text{CH}_2=\text{CMeCOOH}$). By the same method the labile $\text{Et}_2\text{Pb}(\text{OOCMe})_2$ was transformed into the more stable $\text{Et}_2\text{Pb}(\text{OOCCH}_2\text{Cl})_2$.

In 1930 the first organolead sulfonates were obtained by Gilman and Robinson¹²⁴⁸ by heating Et_4Pb with 4- $\text{MeC}_6\text{H}_4\text{SO}_2\text{OH}$ in the presence of silica to form $\text{Et}_3\text{PbOSO}_2\text{C}_6\text{H}_4\text{Me}$ -4. In 1953, Gilman and coworkers¹³⁰⁸ synthesized triethylplumbylsulfonates and sulfinates $\text{Et}_3\text{PbOSO}_2\text{R}$, Et_3PbOSOR from $\text{Et}_3\text{PbOOCMe}$ and the sodium salts of the corresponding acids. In 1936, Schmidt¹³⁰⁴ prepared them by the reaction of Ph_2PbO with sodium pyrocatecholdisulfonate.

Triorganylplumbane and diorganylplumbane esters of oxygen-containing inorganic acids R_3PbX and R_2PbX_2 , where X were the acid anions, could be considered as organolead compounds formally having the plumboxane bond. However, not all of them had a $\text{Pb}-\text{O}-\text{M}$ group with a covalent $\text{Pb}-\text{O}$ bond and so they were properly salts. Particularly, this concerns the derivatives of oxygen-containing strong inorganic acids in which the M atom is highly electronegative (Cl , S , N etc.). For example, organolead ethers of H_2SO_4 and HNO_3 were typical salts. The compounds of this type, i.e. Et_3PbNO_3 ^{43,1217,1218}, $(\text{Et}_3\text{Pb})_2\text{SO}_4$ ^{43,1163,1217,1218} and $[(i\text{-Am})_3\text{Pb}]_2\text{SO}_4$ ^{1217,1218}, were first obtained by Löwig⁴³ (1853), Buckton¹¹⁶³ (1859) and Klippel^{1217,1218} (1860). In 1887, Polis^{1246,1247} first obtained $\text{Ph}_2\text{Pb}(\text{NO}_3)_2$ by the reaction of Ph_2PbCl_2 with AgNO_3 . Compounds such as $\text{Ph}_2\text{Pb}[(\text{OH})\text{CO}_2]_2$, $(\text{Ph}_2\text{Pb})_3(\text{PO}_4)_2$, $\text{Ph}_2\text{PbCrO}_4$, $\text{Ph}_2\text{Pb}(\text{OH})\text{CN}$ and Ph_2PbBr_2 were synthesized by the exchange reactions of $\text{Ph}_2\text{Pb}(\text{NO}_3)_2$ with Na_2CO_3 , Na_3PO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, KCN and KBr , respectively. In 1930, Gilman and Robinson¹²⁴⁸ synthesized $\text{Et}_3\text{PbOPO}(\text{OH})_2$ by heating Et_4Pb with H_3PO_4 . The reaction of aqueous or alcoholic solution of R_3PbOH or $\text{R}_2\text{Pb}(\text{OH})_2$ with the corresponding acids was the

basic method for synthesis of R_3PbA and R_2PbA_2 ($A = \text{acid anion}$). In the past century Tafel¹¹⁴⁴ (1911), Pfeiffer and Trüskier¹²⁴⁹ (1916), Goddard and coworkers⁷²⁸ (1922), Vorlander¹³²⁷ (1925), Buck and Kumro¹³²⁸ (1930), Austin and Hurd^{1256,1262} (1931), Challenger and Rothstein¹³²⁹ (1934), Jones and coworkers¹²⁷¹ (1935), Gilman, Woods and Leeper^{316,1330} (1943, 1951), McCombie and Saunders⁹⁷¹ (1947), Nesmeyanov and coworkers¹¹⁹⁵ (1948), and Saunders and coworkers¹²⁴¹ (1951) synthesized a series of R_3PbA and R_2PbA_2 by this method. In addition, arylsulfonates¹¹⁴⁹ and iodates⁷²⁸ were among the anions in the series given above along with sulfates and nitrates.

G. Compounds having a Pb—S, Pb—Se and Pb—Te Bond

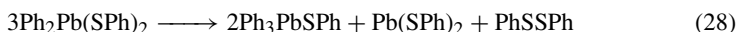
As indicated in Section III. G, according to the Goldschmidt geochemical classification lead as well as tin belong to the chalcophile elements, i.e. they have high affinity to sulfur. Consequently, numerous organolead compounds possessing the plumbathiane Pb—S bond have been easily formed in many reactions involving hydrogen sulfide, alkaline metal sulfides, sulfur and some other sulfurizing agents with various organolead derivatives.

The main organolead derivatives of this type have the following general formulas: $R_3PbSPbR_3$, $(R_2PbS)_n$, $(RPbS_{1.5})_n$, $R_{4-n}Pb(SR')_n$ ($n = 1, 2$). Compounds containing the Pb—S—H bond do not appear in this list, due to their extreme instability. In contrast with isostructural compounds of tin, organolead compounds containing the Pb—S bond attracted only a little attention of researchers and industrial chemists. The number of known compounds of this type, which was less than 50¹³³¹ by 1967, bears witness to this fact. On the one hand this was due to their unacceptability to be used as synthons and reagents, and, on the other hand, due to the seemingly absence of any future practical use. Only a few patents dealing with the application of Me_3PbSMe ^{1332,1333}, $R_3PbSCH_2CONH_2$ ¹³³⁴ and $Me_3PbSPbMe_3$ ¹³³² as potential motor engine antiknocks and the use of compounds $R_3PbSCH_2CONH_2$ ¹³³⁴ and Me_3PbSCH_2COOMe ¹³³⁵ as potential pesticides were issued.

Organolead compounds containing sulfur appeared in chemical circles in the 19th century. The first one was hexaethyldiplumbathiane $Et_3PbSPbEt_3$, which was prepared by Klippel^{1217,1218} employing the reaction of Et_3PbCl with an aqueous solution of Na_2S in 1860. Significantly later, in 1945 the above reaction was repeated at the Calingaert laboratory at 0 °C¹²⁶⁰. It was found during the reaction that $Et_3PbSPbEt_3$ was slowly oxidized by air oxygen to $(Et_3Pb)_2SO_4$. In 1887, Polis¹²⁴⁶ synthesized $(Ar_2PbS)_3$, $Ar = Ph, 4-MeC_6H_4$ by the reaction of $Ar_2Pb(OOCMe)_2$ with H_2S . Only in the second half of the 20th century^{1336–1338} was $(Ph_2PbS)_3$ synthesized again, and it was proved that it was a trimer. Other compounds of the series of $R_3PbSPbR_3$ were obtained in 1911–1917. In 1911, Tafel¹¹⁴⁴ synthesized its representative with $R = i\text{-Pr}$, and its analogs with $R = c\text{-C}_6H_{11}$ and Me were synthesized by Grüttner and Krause^{674,1110}. In 1917, Grüttner and Krause¹¹¹³ obtained $MeEtPbS$, $Pr(i\text{-Bu})PbS$ and $Pr(i\text{-Am})PbS$. At last, in 1918, Grüttner synthesized $Ph_3PbSPbPh_3$ ¹¹¹⁹ for the first time. After this pioneer research no organolead compound having the Pb—S—Pb group was obtained up to 1945. Henry and Krebs^{443,1337} (1963) found that the reaction of Ph_3PbCl with Na_2S proceeded in a different direction with formation of Ph_3PbSNa . The latter interacted with RI ($R = Me, Et$) to give Ph_3PbSR . In 1965, Davidson and coworkers⁴³⁷ obtained $Ph_3PbSPbPh_3$ in a quantitative yield by the reaction of Ph_3PbX ($X = Cl, Br$) with H_2S in the presence of Et_3N or pyridine. Organyl(organylthio)plumbanes $R_{4-n}Pb(SR')_n$ were prepared by the reaction of the corresponding organylhaloplumbanes with mercaptides or thiophenolates of alkali metals or of silver or lead. Saunders and coworkers^{971,1149,1150} first described this type of compound (Et_3PbSEt, Et_3PbSPh) in 1947 and 1949. They were synthesized

by the reaction of Et_3PbOH with RSH or Et_3PbCl with NaSR . These compounds slowly hydrolyze by water and they turned out to be effective sternutators¹³⁰⁴. A convenient method for the synthesis of Ph_3PbSR ($\text{R} = \text{Me, Et, Pr, Bu, Ph, CH}_2\text{Ph, COMe, COPh}$) based on the use of $\text{Pb}(\text{SR})_2$ was elaborated by Krebs and Henry¹³³⁷ (1963) and later applied by Davidson and coworkers⁴³⁷ (1965). This method proved to be unsuitable for the preparation of $\text{Ph}_2\text{Pb}(\text{SR})_2$. These authors⁴³⁷ also attempted to obtain Ph_3PbSR by the cleavage of R_4Pb by thiols, but they were unsuccessful. Compounds of the Ph_3PbSR series turned out to be hydrolytically stable, but it was impossible to distill them without decomposition. This research⁴³⁷ demonstrated that the thermal stability of the M-SR bond in R_3MSR ($\text{M} = \text{Si, Ge, Sn, Pb; R} = \text{Alk, Ar}$) is diminished on increasing the atomic number of M , but their hydrolytic stability had increased. Abel and Brady¹³³⁹ obtained Me_3PbSEt (in 53% yield) by the reaction of Me_3PbCl with EtSH in aqueous NaOH solution in 1965. In 1951, Saunders and coworkers¹²⁴¹ illustrated that the reaction of Et_4Pb with MeCOSH resulted in $\text{Et}_3\text{PbSCOMe}$ and in the presence of silica, in $\text{Et}_2\text{Pb}(\text{SCOMe})_2$, indicating that thiols were capable of cleaving the C-Pb bond.

Davidson and coworkers⁴³⁷ synthesized diphenyl(diorganylthio)plumbanes $\text{Ph}_2\text{Pb}(\text{SR})_2$ by condensation of Ph_2PbX_2 ($\text{X} = \text{Cl, Br}$) with RSH ($\text{R} = \text{Alk, Ar}$) in benzene in the presence of Et_3N or Py as an acceptor of the hydrohalic acids. These compounds appeared to be unstable and decomposed by heating according to equation 28.



By the reaction of Ph_2PbCl_2 with $\text{HSCH}_2\text{CH}_2\text{SH}$ in the presence of Et_3N , 2,2-diphenyl-1,3-dithio-2-plumbacyclopentane⁴³⁷ was obtained. Finally, Davidson and coworkers⁴³⁷ synthesized a series of carbofunctional triphenyl(organylthio)plumbanes $\text{Ph}_3\text{PbS}(\text{CH}_2)_n\text{X}$, where $\text{X} = \text{COOMe, CONH}_2$ ($n = 1$); OH, NH_2 ($n = 2$); $\text{Ph}_3\text{PbSC}_6\text{H}_4\text{X-4}$ ($\text{X} = \text{Cl, NH}_2, \text{NO}_2$) and $\text{Ph}_3\text{PbSC}_6\text{F}_5$. They also prepared the first organolead derivative of a natural hormone, i.e. $\text{Ph}_3\text{PbS-17-}\beta$ -mercaptotestosterone.

The Pb-S bond in trialkylthiocyanatoplumbanes R_3PbSCN was definitely ionic. Klippel^{1217,1218} obtained the first compound of the Et_3PbSCN series by the reaction of Et_3PbCl with AgSCN in alcoholic media as early as 1860. However, Saunders and coworkers^{971,1149} (1947, 1949) could not repeat this reaction. They synthesized the same compound by the reaction of Et_3PbCl with KSCN in alcohol, and Gilman and coworkers¹³⁰⁸ obtained it by the reaction of $\text{Et}_3\text{PbOOCMe}$ with KSCN in 1953. Ethyl(thioacetoxo)plumbanes $\text{Et}_{4-n}\text{Pb}(\text{SCOOMe})_n$ with $n = 1, 2$ were described by Saunders and coworkers¹²⁴¹ in 1951.

Organolead compounds having the Pb-Se and Pb-Te bonds became known only in 1962–1965^{1340–1342}; they were Me_3PbSeMe ^{1341,1342}, Me_3PbSePh ¹³⁴², Ph_3PbSeLi , $\text{Ph}_3\text{PbSePbPh}_3$, Ph_3PbTeLi and $\text{Ph}_3\text{PbTePbPh}_3$ ¹³⁴⁰. The salt-like triethyl(selenocyanato)plumbane was synthesized by Heap and Saunders¹¹⁴⁹ (1949) by the reaction of Et_3PbCl with KSeCN , and by Gilman and coworkers¹³⁰⁸ (1953) by the exchange reaction of $\text{Et}_3\text{PbOOCMe}$ with KSeCN ; it could also be regarded as a compound containing a Pb-Se bond.

In 1961, $\text{R}_3\text{PbSPbR}_3$ ($\text{R} = \text{Alk}$) were proposed as motor fuel antiknocks¹³⁴³.

H. Compounds having a Pb–N Bond

Compounds with a Pb-N bond are the least studied in organolead chemistry. By 1953 there were only less than 10 of them¹⁰⁹. The syntheses of the first representatives of this class were published by McCombie and Saunders^{971,1149} in 1947–1950, but preliminary

reports on their syntheses were given in 1940. These were *N*-trialkylplumbylarene sulfonamides $R_3PbNR'SO_2Ar$, -phthalimides $R_3PbN(CO)_2C_6H_4-o$ ($R = Et, Pr$) and -phthalhydrazides $R_3PbNHN(CO)_2C_6H_4-o$. They were synthesized by the reaction of the corresponding sodium derivatives with R_3PbCl or by the reaction of the free acids or phthalimide with R_3PbOH . In 1953, Gilman and his coworkers¹³⁰⁸ synthesized analogous compounds by reaction of organolead bases R_3PbOH or $(R_3Pb)_2O$ with NH acids such as sulfonamides or imides.

Willemsens and van der Kerk¹¹⁰ applied this method for the synthesis of *N*-trialkylplumbyl-substituted heterocycles containing the endocyclic NH group in 1965. In some cases trialkylhaloplumbanes were also used to synthesize organolead compounds containing the Pb—N bond using reagents containing an N—H bond. In this process an excess of a nitrogen base served as an acceptor of the hydrogen halide^{456,471}.

In the 1950s, some patents were granted for the use of *N*-trialkylplumbyl phthalimide and -phthalhydrazide as fungicides^{1344,1345} and of $Et_3PbNHCHMeEt$ as a herbicide¹³⁴⁶. The latter was obtained by the reaction of Et_3PbCl with $NaNHCHMeEt$. It is remarkable that the preparation of triorganyl(dialkylamino)plumbanes $R_3PbNR'_2$ ($R = Me, Et$) (as well as that of their organotin analogs)¹³⁴⁷ from R_3PbX ($X = Cl, Br$) was successful only when lithium dialkylamides $LiNR'_2$ were used as the aminating agents. This was caused by the ability of triorganylhaloplumbanes (as well as R_3SnX) to form adducts (less stable than the corresponding tin complexes) during the reaction with ammonia and amines but not to substitute the halogen atom by an amino group. Neumann and Kühlein^{1348,1349} first used this method of synthesis in their laboratory in 1966.

The Pb—N bond turned out to be rather active. For example, trialkyl(dialkylamino)plumbanes hydrolyzed extremely rapidly by water, whereas *N*-trialkylplumbyl derivatives of sulfonamides, amides and imides of carboxylic acids as well as their nitrogen heterocycles were hydrolytically rather stable. In the 1960s, the cleavage reactions of the Pb—N bond in $R_3PbNR'_2$ by inorganic and organic acids, alcohols and NH acids (e.g. re-amination by organometallic hydrides) were developed¹³⁵⁰. We shall not consider them here since this period is not yet regarded as historical.

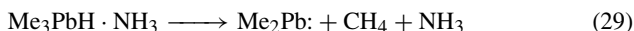
In the 1960s at the Schmidt laboratory^{456,471}, organometallic compounds containing Pb—N—M ($M = Si, Ge$) bonds were synthesized¹³⁵⁰. In 1964, Sherer and Schmidt⁴⁵⁶ obtained trimethylbis(trialkylsilylamino)plumbanes $Me_3PbN(SiR_3)_2$, $R = Me, Et$ by the reaction of Me_3PbCl with $NaN(SiR_3)_2$ ^{456,1351}. Schmidt and Ruidish⁴⁷¹ (1964) prepared analogously $Me_3PbN(GeMe_3)_2$ from $LiN(GeMe_3)_2$.

One year later Sherer and Schmidt¹³⁵² carried out the reaction of Me_3PbCl with $LiN(SiMe_3)_3$, which led to $Me_3PbN(SiMe_3)_3$. In 1961 and 1963 Lieber and coworkers^{1353,1354} synthesized phenylazidoplumbanes $Ph_{4-n}Pb(N_3)_n$ ($n = 1, 2$) from $Ph_{4-n}Pb(OH)_n$ with HN_3 . In 1964, Reichle⁴⁶⁵ reported that, contrary to expectations, Ph_3PbN_3 proved to be rather thermostable and decomposed with formation of Ph_4Pb and N_2 under thermolysis.

The number of organolead compounds having a Pb—N bond reached fifty by 1968¹³⁵⁰.

Pfeiffer and Trüskier¹²⁴⁹ obtained the first organic compounds of hypervalent lead, having coordinated $N \rightarrow Pb$ bonds in 1916. They were isolated during recrystallization of Ph_2PbX_2 ($X = Br, Cl, NO_3$) from pyridine and corresponded to the formula $Ph_2PbX_2 \cdot 4Py$. These complexes were stable only under pyridine atmosphere. In the absence of the latter they lost two molecules of pyridine and transformed into hexacoordinated lead complexes $Ph_2PbX_2 \cdot 2Py$. In ammonia atmosphere Ph_2PbBr_2 formed the unstable complex $Ph_2PbBr_2 \cdot 2NH_3$, which easily lost ammonia¹³⁵⁵. Even these limited data showed that the complexes of organylhaloplumbanes Ph_3PbX and Ph_2PbX_2 with nitrogen bases were unstable and they were not studied further. The preparation of complexes of amines

with RPbX_3 and PbX_4 failed, apparently due to their redox reaction with the addend. Nevertheless, the stable complexes $[\text{Me}_3\text{PbPy}]^+\text{ClO}_4^-$, and $[\text{Me}_2\text{PbPy}_2]_2^{2+}2\text{ClO}_4^-$ and $[\text{Me}_3\text{Pb}(\text{OP}(\text{NMe}_2)_3)_2]^+\text{ClO}_4^-$ were described in 1966. However, they had an ammonium structure, i.e. the lead atom was tetracoordinated but not hypervalent¹³⁵⁶. One should note that, with respect to DMSO, organylhaloplumbanes served as rather strong Lewis acids. In 1966 the stable complexes $\text{Ph}_2\text{PbX}_2 \cdot 2\text{OSMe}_2$ ($\text{X} = \text{Cl}, \text{Br}$) containing hexacoordinated lead atom because of the presence of two $\text{O} \rightarrow \text{Pb}$ bonds¹³⁵⁷ were synthesized. They were so stable that they could be synthesized even in aqueous medium. The melting point of $\text{Ph}_2\text{PbCl}_2 \cdot 2\text{OSMe}_2$, 171°C , witnessed its thermal stability. In 1964, Matviyov and Drago¹³⁵⁸ prepared the complexes of R_3PbCl ($\text{R} = \text{Me}, \text{Et}$) with tetramethylenesulfoxide (B) of compositions $\text{R}_3\text{PbCl} \cdot \text{B}$ and $\text{R}_3\text{PbCl} \cdot 2\text{B}$, $\text{Me}_2\text{PbCl}_2 \cdot 2\text{B}$ and $\text{R}_3\text{PbCl}_2 \cdot 4\text{B}$. $\text{Me}_3\text{PbCl} \cdot \text{B}$ had a trigonal-bipyramidal structure, i.e. its lead atom was pentacoordinated. The second and third complexes were apparently of octahedral structure and in $\text{Me}_2\text{PbCl}_2 \cdot 4\text{B}$ the lead atom was octacoordinated. Later, the analogous complex $[\text{Me}_2\text{Pb}(\text{OSMe}_2)_4](\text{ClO}_4)_2$ was obtained. In 1961, Duffy and Holliday¹³⁵⁹ showed that the reaction of Me_3PbCl with KBH_4 in liquid NH_3 at -70°C led to an adduct of $\text{Me}_3\text{Pb}(\text{BH}_4) \cdot n\text{NH}_3$ composition with $n \geq 2$ (probably, it was a mixture of $\text{Me}_3\text{PbH} \cdot \text{NH}_3$ and $\text{H}_3\text{N} \cdot \text{BH}_3$). The product obtained at -5 to $+20^\circ\text{C}$ decomposed with the formation of Me_3PbH , NH_3 and $\text{H}_3\text{N} \cdot \text{BH}_3$. The Me_3PbH obtained reacted instantly with liquid ammonia at -78°C with the formation of an unstable green adduct, which evidently was $\text{Me}_3\text{PbH} \cdot \text{NH}_3$. Based on the ^1H NMR data, the authors ascribed to the product the very unlikely structure of ammonium trimethylplumbate Me_3PbNH_4 containing the Me_3Pb^- anion. This complex evolved CH_4 and NH_3 at -78°C and was slowly transformed into $\text{Me}_3\text{PbPbHMe}_2 \cdot \text{NH}_3$, which in the authors' opinion provided the red color of the reaction mixture. However, it was most probably Me_2Pb , which provided the red color according to equations 29 and 30.



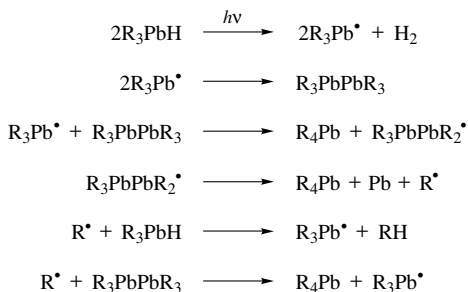
Pentamethyldiplumbane ammoniate decomposed to Me_4Pb , $\text{Me}_3\text{PbPbMe}_3$, CH_4 , H_2 and Pb at -45°C . The solution of Me_3PbH in Me_3N was less stable than its solution in liquid ammonia.

I. Organolead Hydrides

The first investigations of organolead hydrides $\text{R}_{4-n}\text{PbH}_n$ ($n = 1, 2$) were conducted only in the 1960s. The reason for their late appearance was their extreme instability due to the presence of the $\text{Pb}-\text{H}$ bond. Early attempts to obtain organolead hydrides R_3PbH by the reaction of R_3PbNa ($\text{R} = \text{Et}, \text{Ph}$) with NH_4Br in liquid ammonia^{1170,1360} or by catalytic hydrogenation of $\text{Ph}_3\text{PbPbPh}_3$ had failed. In 1958, Holliday and Jeffers¹³⁶¹ were the first to report the preparation of Me_3PbH , when they found that it was formed by decomposition of Me_3PbBH_4 in liquid ammonia. Later, Duffy and Holliday^{1359,1362,1363} used the reduction reaction of R_3PbCl by KBH_4 in liquid ammonia to prepare R_3PbH ($\text{R} = \text{Me}, \text{Et}$). An intermediate of this reaction was R_3PbBH_4 , which eliminated R_3PbH at -5°C . In 1960, Amberger¹³⁶⁴ synthesized R_3PbH and R_2PbH_2 ($\text{R} = \text{Me}, \text{Et}$) by the reduction of the appropriate organolead chlorides by LiAlH_4 in Me_2O . Becker and Cook¹²¹² (1960) used for this purpose the reaction of R_3PbX ($\text{X} = \text{Cl}, \text{Br}$) with KBH_4 in liquid ammonia or with LiAlH_4 in Me_2O at -78°C . Dickson and West¹³⁶⁵ succeeded in obtaining some amount of Et_3PbH by the decomposition of Et_3PbNa by ammonium bromide in liquid ammonia in 1962.

Neumann and Kühlein^{1213,1366} used the reduction of R_3PbCl by $LiAlH_4$ for the synthesis of R_3PbH , $R = Pr, Bu, i-Bu, c-C_6H_{11}$ in 1965. They also synthesized Bu_2PbH_2 from Bu_2PbCl_2 . Such solvents as Me_2O , Et_2O , THF or diglyme, which interacted with the $AlCl_3$ formed, were used for this purpose since the $AlCl_3$ caused decomposition of the R_3PbH ^{1212,1317,1366}. In 1966, Amberger and Hönigschmid-Grossich¹³⁶⁷ demonstrated that trialkylmethoxyplumbanes R_3PbOMe reacted with B_2H_6 at $-35^\circ C$ to form R_3PbBH_4 . Further treatment at $-78^\circ C$ by $MeOH$ resulted in R_3PbH with $R = Me, Et, Pr, Bu$. Even without methanolysis, Me_3PbBH_4 slowly decomposed in ether with formation of Me_3PbH at $-78^\circ C$ ¹³⁶². In 1965, Neumann and Kühlein^{1213,1366} showed that Et_3PbCl could be reduced by Bu_3PbH to Et_3PbH , which was removed from the reaction mixture by distillation. High-boiling organotin hydrides R_3SnH and R_2SnHCl ($R = Bu, Ph$) were employed as reductants of Et_3PbX . Thus, within the period from 1960 till 1965, 10 organolead hydrides were synthesized. The low organolead hydrides $R_{4-n}PbH_n$ ($R = Me, Et; n = 1, 2$) were liquids, which decomposed at temperatures below $0^\circ C$ ^{1212,1367}. Duffy and coworkers¹³⁶³ (1962) identified methane as a gaseous product of the Me_3PbH decomposition. According to Amberger and Hönigschmid-Grossich¹³⁶⁷ high trialkylplumbanes started to decompose to R_4Pb , R_3PbPbR_3 , Pb and H_2 ¹³⁶⁷ without air in vacuum at -30 to $-20^\circ C$. Neumann and Kühlein^{1213,1366} showed in 1965 that Pr_3PbH was completely decomposed (disproportionated) to Pr_4Pb , $Pr_3PbPbPr_3$, Pb , C_3H_8 and H_2 ¹³⁶⁶ within 24 hours. Propane appeared in the product of the hydrogen atom cleavage from Pr_3PbH .

Becker and Cook¹²¹² (1960) proposed a rather complicated scheme for the homolytic decomposition of R_3PbH (Scheme 1). It was possible that this process was simpler, involving the intermediate formation of PbR_2 .



SCHEME 1

In 1960, Becker and Cook¹²¹² were the first to succeed in carrying out the reaction of hydroplumbylation (a term first suggested by Voronkov in 1964⁵³). They demonstrated that Me_3PbH was added to ethylene in diglyme at 35 atm and $0^\circ C$ with the formation of Me_3PbEt in 92% yield. Unlike that, Duffy and coworkers¹³⁶³ found that trialkylplumbanes did not add to ethylene in Me_2O media or without solvent at normal pressure. Neumann's¹³⁶⁶ attempts to carry out the hydroplumbylation reaction of $CH_2=CHR$ ($R = C_6H_{13}, CH_2OH, CH_2OOCMe$) with Bu_3PbH at $0^\circ C$ or $20^\circ C$ were unsuccessful as well. Nevertheless, Blitzer and coworkers¹³⁶⁸ patented a method of addition of organolead hydrides to terminal olefins and cyclohexene in 1964. In 1965, Neumann and Kühlein^{1213,1366} found that Bu_3PbH was added to compounds having terminal activated double bonds $CH_2=CHR$ ($R = CN, COOMe, Ph$) at $0^\circ C$. In 1965, Leusink and van der Kerk¹²¹⁴ showed that Me_3PbH added easily to $HC\equiv C-CN$ and $HC\equiv C-COOMe$.

The *cis*-adduct was the first product of the hydroplumbylation of cyanoacetylene and it was consequently converted into the *trans*-isomer at temperatures from -78°C to 0°C . At about the same time Neumann and Kühlein¹²¹³ carried out a similar reaction of Bu_3PbH with $\text{HC}\equiv\text{CPh}$ that led to the *trans*-adduct. They also showed that Bu_3PbH did not add to the $\text{C}=\text{O}$ bonds of aldehydes and ketones. In contrast, they showed that in the reaction of Bu_3PbH with $\text{PhN}=\text{C}=\text{S}$ the hydroplumbylation of thiocarbonyl group proceeded with the formation of $\text{Bu}_3\text{PbS}-\text{CH}=\text{NPh}$. They also found that $\text{Bu}_3\text{PbN}(\text{CH}=\text{O})\text{Ph}$, the product of the $\text{N}=\text{C}$ bond hydroplumbylation, was formed in the reaction of Bu_3PbH with $\text{PhN}=\text{C}=\text{O}$ at -70°C . Phenylisocyanurate $(\text{PhNC}=\text{O})_3$ and $\text{Bu}_3\text{PbPbBu}_3$ were the final products of the reaction. In 1968, Neumann and Kühlein¹³⁶⁹ investigated the mechanism of the hydroplumbylation reaction, which was found to proceed by both radical and ionic processes.

In 1960, Becker and Cook¹²¹² pointed out that $\text{R}_{4-n}\text{PbH}_n$ ($\text{R} = \text{Me, Et; } n = 1, 2$) reacted with diazoalkanes $\text{R}'\text{CHN}_2$ ($\text{R}' = \text{H, Me}$) with the formation of both the products of hydrides disproportionation and the insertion of the $\text{R}'\text{CH}$ group into the $\text{Pb}-\text{H}$ bond from -80 to -0°C .

Duffy and coworkers^{1359,1363} found that R_3PbH ($\text{R} = \text{Me, Bu}$) were decomposed under ammonia and amines action. Trimethylplumbane reacted with liquid ammonia to give green and then red solutions (evidently connected with an intermediate formation of Me_3Pb^+ and Me_2Pb) and Me_4Pb , Pb and CH_4 were formed. Addition of PbCl_2 to an Me_3PbH solution in NH_3 led to $\text{Me}_3\text{PbPbMe}_3$ in almost a quantitative yield¹³⁵⁹. Organolead hydrides were extremely easily oxidized by air oxygen (Me_3PbH was oxidized with an explosion)¹²¹² and they turned out to be strong reductants (more effective than organic hydrides of Ge and Sn). In 1960, Neumann¹³⁷⁰ found that trialkylplumbanes reacted with ethyl iodide even at temperatures from -60 up to -40°C with the formation of ethane. Holliday and coworkers¹³⁶³ (1962) found that Me_3PbH reacted with HCl to give Me_3PbCl and H_2 as well as some amount of $\text{Me}_3\text{PbPbMe}_3$ at -112°C . Along with them Me_2PbCl_2 and CH_4 were identified at -78°C .

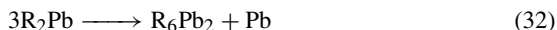
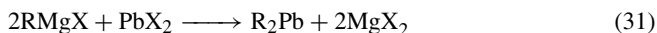
In 1965, Neumann and Kühlein^{1213,1366} reduced aliphatic halogens, and carbonyl, nitro and nitroso compounds, and Et_3SnCl as well, by tributylplumbane at 0°C and 20°C . A higher temperature was found unacceptable due to the decomposition of Bu_3PbH .

J. Compounds Containing a Pb—Pb Bond

Almost all the known compounds having a $\text{Pb}-\text{Pb}$ bond are hexaorganyldiplumbanes R_3PbPbR_3 and only a few of them do not correspond to this formula. Hexaorganyldiplumbanes have been regarded for a long time as trivalent lead derivatives and it is a wonder that even such leaders of metalloorganic chemistry as Gilman (with Towne) in 1939¹²⁵⁴ and Kocheshkov in 1947¹⁵⁶ and with Panov even in 1955¹³¹³ gave the R_3Pb formula to these compounds. Some historical aspects and data concerning the synthesis and transformations of hexaorganyldiplumbanes were given in Sections IV.B, IV.C and IV.E because they were connected with the quoted data. Herein we consider the historical developments of the investigations of compounds having the $\text{Pb}-\text{Pb}$ bond in more detail.

As reported in Section IV.B, Löwig⁴³ obtained hexaethylplumbane, the first organolead compound having the $\text{Pb}-\text{Pb}$ bond, in 1953. It was difficult to decide whether this compound was Et_6Pb_2 (Et_3Pb radical by Löwig) or Et_4Pb according to his data, which were based on the atomic weights known at that time. In 1859, Buckton¹³⁷¹ reported that the compound described by Löwig was apparently Et_4Pb and this was confirmed by Ghira¹³⁷² in 1894. Moreover, he stated: 'At the present time no lead compounds of the type PbX_3 or Pb_2X_6 have ever been reported, studied or isolated.'

In 1919, Krause and Schmitz¹¹²⁰ obtained for the first time hexaaryldiplumbane $\text{Ar}_3\text{PbPbAr}_3$ ($\text{Ar} = 2,5\text{-Me}_2\text{C}_6\text{H}_3$) by the reaction of $2,5\text{-Me}_2\text{C}_6\text{H}_3\text{MgBr}$ with PbCl_2 . In 1921, Krause¹¹²¹ synthesized hexacyclohexyldiplumbane analogously. He wrote that tetracyclohexylplumbane which was obtained by Grüttner⁶⁷⁴ in 1914 was apparently nonpure. The synthesis of R_3PbPbR_3 from RMgX and PbCl_2 was further used by Krause and Reissaus^{1122,1292} (1921, 1922), Calingaert and coworkers^{1188,1373} (1938, 1942) and Gilman and Bailie¹¹⁷⁰ (1939). It was established that R_2Pb were the labile intermediates of this reaction, which is described by equations 31 and 32.



Hexaethyldiplumbane, whose chemical composition and structure were unequivocally proved, was obtained by electrolysis of Et_3PbOH with lead cathode in alcoholic medium by Calingaert and coworkers¹¹⁴⁰ only in 1923. The electrochemical method for the R_3PbPbR_3 synthesis was further developed by the Calingaert group^{1188,1373} in 1938–1942 and by Italian chemists¹³⁷⁴ in 1960. In 1960, Vyazankin and coworkers¹²⁰³ found that during the electrochemical synthesis of $\text{Et}_3\text{PbPbEt}_3$ a new product, identified as Et_2Pb , was formed along with it. Hein and Klein¹²⁰¹ found that compounds R_3PbPbR_3 ($\text{R} = \text{Me}$, Et) were easily formed by the reduction of R_3PbCl by Al , Zn or Pb in alkaline solution. In the years 1938 and 1939, the method for R_3PbPbR_3 synthesis based on the reaction of R_3PbX ($\text{R} = \text{Alk}$, Ar ; $\text{X} = \text{Cl}$, Br , I) with Na in liquid ammonia^{791,1170,1188,1189} began to develop. This fact was more surprising since even in 1947 Kocheshkov related to the formation of R_3PbPbR_3 from a reduction of R_3PbX to R_3Pb ¹⁵⁶. He referred to the magnetochemical evidence of this fact given by Preckel and Selwood in 1940¹³⁷⁵.

Bright red tetrakis(triphenylplumbyl)plumbane $(\text{Ph}_3\text{Pb})_4\text{Pb}$ obtained by the simultaneous hydrolysis and oxidation of Ph_3PbLi or Ph_2Pb by H_2O_2 at low temperature by Willemsens and van der Kerk^{109,1376,1377} turned out to be the first organolead compound having several Pb-Pb bonds. Tetrakis(triphenylplumbyl)plumbane was an unstable compound which decomposed into $\text{Ph}_3\text{PbPbPh}_3$ and Pb at storage. This indicated that the Pb-Pb-Pb bond system was quite unstable.

Gilman and Woods¹³³⁰ and Leeper¹³⁷⁸ in 1943 and Gilman and Leeper in 1951³¹⁶ described the condensation of diorganyldihaloplumbanes with lithium and calcium. Foster and coworkers¹¹⁸⁹ (1939) carried out the reaction of Ph_3PbCl with $[\text{Na}_4\text{Pb}_9]$.

For the synthesis of hexaaryldiplumbanes Gilman and coworkers^{1170,1185} (1939, 1952) and Podall and coworkers¹³⁷⁹ (1959) used lithium aryls. In 1941, Bindschadler¹¹⁹⁰ obtained hexaphenyldiplumbane by the reaction of Ph_3PbNa with $\text{BrCH}_2\text{CH}_2\text{Br}$. Hein and Nebe¹¹⁸⁷ synthesized hexacyclohexyldiplumbane by the reaction of $(c\text{-C}_6\text{H}_{11})_3\text{PbNa}$ with mercury. In 1931, Goldach¹¹⁴⁷ found that hexaisopropyldiplumbane was formed by the reaction of acetone with a Na-Pb alloy in sulfuric acid. Hexamethyldiplumbane was isolated by the reaction of Me_3PbCl with the adduct $\text{Me}_3\text{PbH} \cdot \text{NH}_3$ in liquid ammonia by Duffy and Holliday¹³⁵⁹. In 1962, the same authors¹³⁶³ observed that $\text{Me}_3\text{PbPbMe}_3$ was the product of the thermal dehydrocondensation of Me_3PbH . In the first half of the 20th century, twenty hexaorganyldiplumbanes were synthesized by the methods described above.

All hexaalkyldiplumbanes described in the literature turned out to be thermally unstable liquids which decomposed on distillation. In 1923, Calingaert and coworkers reported that $\text{Et}_3\text{PbPbEt}_3$ dissociated into the $\text{Et}_3\text{Pb}^{\bullet}$ radicals in dilute solutions¹¹⁴⁰. However, in concentrated solutions $\text{Et}_3\text{PbPbEt}_3$ was the main species. The molecular weights found for R_3PbPbR_3 with $\text{R} = \text{Ph}$ ^{1336,1380,1381}, $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ¹³⁸² and $c\text{-C}_6\text{H}_{11}$ ¹³⁸⁰ showed that

all the compounds corresponded to the formula given above. In particular, the thermolysis data of $\text{Et}_3\text{PbPbEt}_3$ obtained by Razuvaev and coworkers^{1202,1295,1300,1383} and other investigations^{984,1239,1384} corroborated the structure.

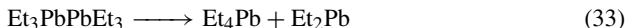
In contrast, hexaaryldiplumbanes were crystalline substances and were successfully purified by recrystallization.

All the R_3PbPbR_3 disproportionated with the formation of R_4Pb in up to 90% yields¹¹⁷⁰ and to Pb during the thermolysis. The starting temperature for this process depended on the nature of R. As for hexaalkyldiplumbanes, Calingaert and coworkers¹³⁷³ (1942) reported that they similarly decomposed even on distillation. According to Krause and Reissaus¹¹²² (1922), hexaaryldiplumbanes decomposed around their melting points of 117°C ($\text{R} = 3\text{-MeC}_6\text{H}_4$) and 255°C ($\text{R} = 1\text{-C}_{10}\text{H}_7$, 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$). Gilman and Bailie¹¹⁷⁰ (1939) found that the thermal stability of R_3PbPbR_3 increased in the following order for R: $\text{Me} < \text{Et} < \text{Ph} < 3\text{-MeC}_6\text{H}_4 < 4\text{-MeC}_6\text{H}_4 < 4\text{-MeOC}_6\text{H}_4 < 4\text{-EtOC}_6\text{H}_4 \ll 2\text{-MeC}_6\text{H}_4 < 2\text{-MeOC}_6\text{H}_4 < 2\text{-EtOC}_6\text{H}_4 < c\text{-C}_6\text{H}_{11}$, 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2 < 1\text{-C}_{10}\text{H}_7$.

In 1951–1963, a number of investigations established that the thermolysis of hexaorganyldiplumbanes is catalyzed by silica¹²⁹⁸ (1951), activated charcoal¹²⁹⁹ (1956), AlCl_3 ¹²⁹⁵ (1960), as well as by lead, which is formed during the thermolysis process¹³⁰⁰ (autocatalysis) and also by UV irradiation¹²³⁷ (1963).

In 1960, Razuvaev, Vyazankin and Chshepetkova⁹⁰³ found that $\text{Et}_3\text{PbPbEt}_3$ decomposed with a Pb–Pb bond cleavage in the presence of a catalytic amount of free-radical initiators such as benzoyl peroxide or tetraacetoxylumbane at room temperature.

In 1942, Calingaert and coworkers¹³⁷³ showed that the 1 : 1 $\text{Me}_3\text{PbPbMe}_3\text{--Et}_3\text{PbPbEt}_3$ system gave at 100°C a mixture of tetraalkylplumbanes of the following composition (%): Me_4Pb (18), Me_3PbEt (15), Me_2PbEt_2 (23), MePbEt_3 (31), Et_4Pb (13). The yield of lead was 5% of the theoretical calculated value. These data indicated that during the thermolysis of hexaalkyldiplumbanes, alkyl radicals, the corresponding Pb-centered free radicals as well as dialkylplumbylenes Alk_2Pb were formed. Indeed, in 1959 Razuvaev and coworkers¹²⁰² established that the thermal decomposition of hexaethyldiplumbane proceeded in accordance with equations 33 and 34.



One year later¹²⁰³ they also studied the kinetics of the thermolysis of mixtures of $\text{Et}_3\text{PbPbEt}_3$ with Et_4Pb or with Et_2Pb at 135°C. The data confirmed that the process proceeded according to equations 33 and 34. As a result of their investigations they concluded that the thermal decomposition of $\text{Et}_3\text{PbPbEt}_3$ was different from its disproportionation reaction, which occurred in the presence of catalysts.

In 1962, Razuvaev and coworkers¹³⁸³ studied the decomposition of $\text{Ph}_3\text{PbPbPh}_3$ in solutions and in the presence of metal salts. Krebs and Henry¹³³⁷ studied the same reaction in boiling MeCOOH . Belluco and Belluco¹³⁸⁵ used a radiochemical method to show that the intermediate of the thermolysis was diphenylplumbylene Ph_2Pb . As early as 1860 Klippel^{1217,1218} observed the photochemical decomposition of hexaorganyldiplumbanes. He found that $\text{Et}_3\text{PbPbEt}_3$ decomposed under light and isolated metallic lead.

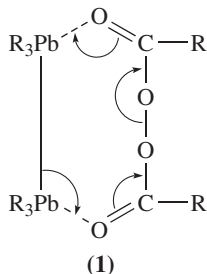
In 1919, Krause and Schmitz¹¹²⁰ observed that the yellow color of the solution of R_3PbPbR_3 ($\text{R} = 2,4\text{-Me}_2\text{C}_6\text{H}_3$) quickly disappeared under sunlight to give a white precipitate. They concluded that the compound obtained decomposed under light irradiation. Two years later Krause¹¹²¹ reported that hexacyclohexyldiplumbane was also decomposed by light, but it was absolutely stable in the dark. According to Krause and Reissaus^{1122,1292} its molecular weight was decreased when it was diluted in benzene. Analogously, the

molecular weights of R_3PbPbR_3 with $R = Ph$ and $4-MeC_6H_4$ depended on the concentration of their solutions. In 1923, Calingaert and coworkers¹¹⁴⁰ reached the same conclusion. Lesbre and coworkers¹¹⁷¹ determined cryoscopically the molecular weight of hexamethyldiplumbane. However, EPR data indicated that this compound did not dissociate into free radicals R_3Pb^\bullet ¹³⁸² in benzene. An EPR study of R_3PbPbR_3 in the crystal and in solutions in C_6H_6 and $CHCl_3$ also did not detect any dissociation into free radicals¹³⁸⁵. Willemsens¹⁰⁹ tried to ascribe the difference between the EPR and the cryoscopic data to the imperfection of the latter method. However, this explanation does not stand up to criticism because an analogous decrease of the molecular weight in dilute solutions of hexaorganyldistannanes R_3SnSnR_3 was established as well by ebullioscopy (see Section III.H). It must be assumed that the decrease of the molecular weight of hexaorganyldiplumbanes in dilute solutions was not caused by their dissociation into free radicals R_3Pb^\bullet , but was caused by their decomposition into R_4Pb and R_2Pb . In accordance with that, Razuvaev and coworkers¹²⁰² observed that the concentration of Et_4Pb , which was usually presented in $Et_3PbPbEt_3$ increased with time.

A pale yellow or pink color¹⁰⁹ indicated the presence of R_2Pb in the solution of R_3PbPbR_3 in organic solvents.

In 1943, Hein and coworkers¹³¹⁴ studied the auto-oxidation process of hexacyclohexyldiplumbanes and found that it took place only under ultraviolet irradiation. Obviously, this observation allowed Peters¹³⁸⁶ to patent the use of this compound for the preparation of photosensitive films in 1961. In 1961–1963, Aleksandrov and coworkers^{1310,1387,1388} investigated in detail the oxidation of $Et_3PbPbEt_3$ by oxygen at low temperatures. The final products of this reaction were Et_3PbOH , C_2H_6 , C_2H_4 and PbO , and $Et_3PbOPbEt_3$ was the intermediate. Aleksandrov and coworkers¹³⁰³ (1959) studied the oxidation of $Et_3PbPbEt_3$ by α -hydroperoxoisopropylbenzene $HOOCMe_2Ph$ and 1,4-bis(α -hydroperoxoisopropyl)benzene 1,4- $(HOOCMe_2)_2C_6H_4$, which led to Et_3PbOH formation. In the first case $Et_3PbOOCMe_2Ph$ and in the second $(Et_3PbOOCMe_2)_2C_6H_4$ were formed. The two compounds were the first organolead peroxides. The reaction of $Et_3PbPbEt_3$ with $Et_3PbOOCMe_2Ph$ led to $Et_3PbOPbEt_3$ and $Et_3PbOCMe_2Ph$. The oxidation product of hexaethyldiplumbane by benzoyl peroxide was $Et_3PbOOCPh$. In 1960, Razuvaev and coworkers⁹⁰³ found that the $Pb-Pb$ bond in $Et_3PbPbEt_3$ was cleaved by $MeCOOH$ to give $Et_3PbOOCMe$.

The reactions studied above were nonradical because they could not be initiated by AIBN. This suggested that a concerted cleavage of the $Pb-Pb$ bond took place in the cyclic intermediate as shown in structure **1**. According to Austin¹²⁵³ (1931) and Bähr¹²⁵⁵ (1947), the R_3PbPbR_3 oxidation by $KMnO_4$ led to R_3PbOH . In 1959, Podall and coworkers¹³⁷⁹ established that the hydrogenolysis of $Ph_3PbPbPh_3$ led to metallic lead formation, as well as to Ph_4Pb or Ph_2 (depending on the reaction conditions and the catalyst used).

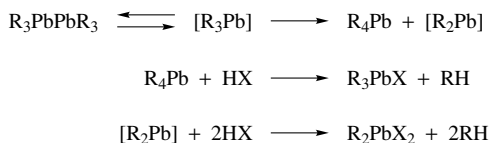


As early as in 1856, Klippel^{1217,1218} carried out the Pb–Pb bond cleavage by halogens. He found that hexaethyl- and hexaisoamyldiplumbane reacted easily with iodine in ether, to form R_3PbI ($R = Et, i-Am$). In 1919, Krause and Schmitz¹¹²⁰, by reacting R_3PbPbR_3 ($R = 2,5-Me_2C_6H_3$) with bromine, confirmed that hexaorganyldiplumbanes decomposed by halogens. When pyridine was used as the solvent, R_3PbBr was formed, but when chloroform was used the product was R_2PbBr_2 . After 2–3 years, in the Krause laboratory, the cleavages of R_3PbPbR_3 by bromine or iodine when $R = c-C_6H_{11}$ ¹¹²¹, Ph or $4-MeC_6H_4$ ¹¹²² were studied and the corresponding R_3PbX ($X = Br, I$) were obtained in good yield. In the period 1931–1961, some reports had appeared about the halogenation of the R_3PbPbR_3 series with $R = Ar$ ^{791,1170,1389}, $PhCH_2CH_2$ ⁸³³, $c-C_6H_{11}$ ^{791,1187}. Depending on the reaction conditions R_3PbX , R_2PbX_2 and PbX_2 were prepared in different ratios.

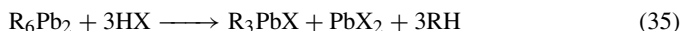
In 1964, Willemsens and van der Kerk¹³⁷⁷ found that reaction of $(Ph_3Pb)_4Pb$ with iodine led to Ph_3PbI and PbI_2 , thus confirming the branched structure of the compound. Remarkably, even in 1947 Kocheshkov¹⁵⁶ considered the Pb–Pb bond cleavage in R_3PbPbR_3 as an oxidation reaction of trivalent lead (R_3Pb) which gave the tetravalent R_3PbX derivatives.

In 1923, Calingaert and coworkers¹¹⁴⁰ showed that $Et_3PbPbEt_3$ was cleaved by HCl with the formation of Et_3PbCl , $PbCl_2$ and C_2H_6 . In 1931, Austin¹²⁶² obtained $(2-MeC_6H_4)_3PbBr$ by the cleavage of hexa-*ortho*-tolylldiplumbane by HBr.

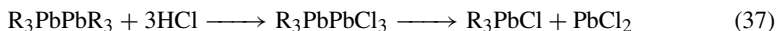
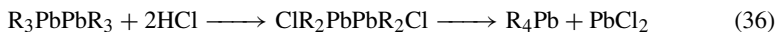
In 1939, the R_3PbPbR_3 cleavage by hydrohalic acids was frequently used to form R_3PbX ^{791,1170,1254}. Belluco and coworkers¹³⁹⁰ (1962) as well as Krebs and Henry¹³³⁷ (1963) concluded that the reaction of R_3PbPbR_3 with hydrohalic acid was not a single-stage process because R_3PbH was not formed. In their opinion, the process was more complicated and could be described by Scheme 2 (for $X = Cl$). The general equation of the process was equation 35.



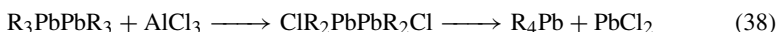
SCHEME 2



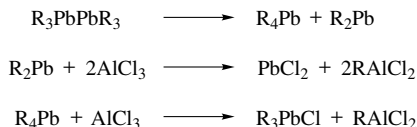
In 1964, Emeleus and Evans¹³⁹¹ found that the C–Pb bond was the first to be cleaved and the Pb–Pb bond was cleaved next in the reactions of HCl with R_3PbPbR_3 . The process of formation of $PbCl_2$ was unclear and hence the reaction mechanism was represented by the two equations 36 and 37.



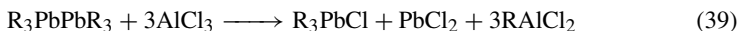
The data of Gilman and Apperson¹²³⁹ (1939) served as proof of the intermediate formation of ClR_2PbPbR_2Cl , so they proposed that the reaction of R_3PbPbR_3 with $AlCl_3$ could be described by equation 38.



According to a later point of view of Gilman and coworkers¹¹²⁹, the mechanism of the reaction of hexaorganyldiplumbanes with aluminum chloride can be represented by Scheme 3, which is summarized by equation 39.



SCHEME 3



Scheme 3 did not require the initial cleavage of the C—Pb bond by AlCl_3 as well as the intermediate formation of $\text{ClR}_2\text{PbPbR}_2\text{Cl}$, which has not yet been identified.

In 1952, Kocheshkov and Panov¹²⁸¹ found that $\text{Ar}_3\text{PbPbAr}_3$ ($\text{Ar} = 4\text{-MeC}_6\text{H}_4$) was cleaved by HNO_3 to form Ar_3PbNO_3 . An excess of HNO_3 led to $\text{Ar}_2\text{Pb}(\text{NO}_3)_2$.

Razuvaev and coworkers⁹⁰³ showed that $\text{Pb}(\text{OOCMe})_4$ cleaved $\text{Et}_3\text{PbPbEt}_3$ in benzene media with a formation of $\text{Et}_3\text{PbOOCMe}$ in 1960. In 1963, Krebs and Henry¹³³⁷ found that the Pb—Pb bond in R_3PbPbR_3 was cleaved by the reaction of MeCOOH , MeCOSH , S and $\text{BrCH}_2\text{CH}_2\text{Br}$. In 1943, Hein and coworkers¹³¹⁴ studied the reaction of hexacyclohexyldiplumbane with polyhalomethanes. The organolead products of this reaction were R_3PbX , R_2PbX_2 ($\text{R} = \text{c-C}_6\text{H}_{11}$) and PbX_2 .

Krohn and Shapiro¹³⁹² (1951) patented the cleavage reaction of R_3PbPbR_3 by alkyl halides as a method for the preparation of R_4Pb ($\text{R} = \text{Alk}$) in a high yield from R_3PbPbR_3 and RX ($\text{X} = \text{Br}, \text{I}$) at $20\text{--}100^\circ\text{C}$. In 1960, Razuvaev, Vyazankin and their coworkers^{1293,1389} investigated thoroughly the reaction of hexaethyldiplumbane with organobromides. They found that the reaction of $\text{Et}_3\text{PbPbEt}_3$ with EtBr , $\text{BrCH}_2\text{CH}_2\text{Br}$ and $\text{BrCH}_2\text{CHBrCH}_3$ led to Et_4Pb as well as to Et_3PbBr , Et_2PbBr_2 , PbBr_2 and Pb in heptane media at $40\text{--}70^\circ\text{C}$. When used in catalytic amounts, the bromides initiated the disproportionation of $\text{Et}_3\text{PbPbEt}_3$ into Et_4Pb and Pb .

In 1860, Klippel^{1217,1218} found that the reaction of $\text{Et}_3\text{PbPbEt}_3$ with AgNO_3 in alcoholic media led to Et_3PbNO_3 and metallic silver. According to Krause and Grosse¹⁵⁵, during the reaction of hexaorganyldiplumbanes with AgNO_3 in alcohols at low temperature the reaction mixture became green colored, which was attributed to the formation of R_3PbAg . In 1960–1961, Belluco and coworkers¹³⁷⁴ and Duffy and Holliday¹³⁵⁹ studied the reaction of $\text{Et}_3\text{PbPbEt}_3$ with an alcoholic solution of AgNO_3 at room temperature, from which triethylplumbyl nitrate and metallic silver were isolated. Thus, they reproduced the results of Klippel^{1217,1218} one hundred years later.

In 1931–1962 the reactions of the R_3PbPbR_3 cleavage by chlorides of Cu ^{1393,1394}, Au ¹³⁹⁴, Hg ¹³⁹⁴, Al ^{1239,1395}, Ti ¹¹⁷⁶ and Fe ^{1256,1394} were studied. In 1939, Gilman and Bailie¹¹⁷⁰ found that sterically hindered R_3PbPbR_3 with $\text{R} = 2\text{-MeC}_6\text{H}_4$, $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ and $\text{c-C}_6\text{H}_{11}$ were cleaved with MgI_2 (Mg itself did not apparently exhibit any effect) giving R_3PbI . Unlike this, the reaction of R_3PbPbR_3 having no bulky substituents with a $\text{MgI}_2\text{--Mg}$ system led to R_4Pb , Pb and RMgI . Probably, it proceeded through an intermediate formation of R_3PbI and R_2Pb . In 1963, Belluco and coworkers¹³⁹⁶ studied the cleavage of $\text{Et}_3\text{PbPbEt}_3$ by chlorides and oxychlorides of sulfur. It was found that the yield of Et_3PbCl was lower as the nucleophilicity of the sulfur atom increased, i.e. in the order: $\text{SO}_2\text{Cl}_2 > \text{SOCl}_2 > \text{SCl}_2 > \text{S}_2\text{Cl}_2$.

An unexpected addition of R_3PbPbR_3 to multiple bonds was reported by Gilman and Leeper³¹⁶ in 1951. They suggested that the reaction of $Ph_3PbPbPh_3$ with maleic anhydride led to 2,3-bis(triphenylplumbyl)succinic anhydride. However, in 1964, Willemsens¹⁰⁹ noted that the product of the reaction was apparently diphenylplumbylen maleate formed from an admixture of maleic acid, which was present in its anhydride. This conclusion was corroborated by the absence of any reaction of $Ph_3PbPbPh_3$ with pure maleic anhydride. The formation of diphenylplumbylenmaleate (along with Ph_4Pb) was assumed to result from decomposition of an intermediate product bis(triphenylplumbyl) maleate.

In 1941, Bindschadler and Gilman¹¹⁸² showed that $PhLi$ cleaved $Ph_3PbPbPh_3$ with formation of Ph_3PbLi and Ph_4Pb . Gilman and Bailie^{791,1170} (1939) and Foster and coworkers¹¹⁸⁹ (1939) found that the reaction of $Ar_3PbPbAr_3$ with Na in liquid ammonia led to Ar_3PbNa , whose solution was dark-red colored. It was found in 1941–1953 that hexaphenyldiplumbane was similarly cleaved by alkali and alkali earth metals (Li, K, Rb, Ca, Sr, Ba) in liquid ammonia at the Gilman^{316,1182,1378} laboratory. Hein and coworkers^{118,1397} (1942, 1947) found that sodium in ether media cleaved hexacyclohexyldiplumbane. In 1962, Tamborski and coworkers¹³⁹⁸ showed that $Ph_3PbPbPh_3$ was cleaved by Li in THF to form Ph_3PbLi in a high yield.

In 1922, Krause and Reissaus¹¹²² succeeded in isolating two monomers of diarylplumbylenes Ar_2Pb ($Ar = Ph, 2-MeC_6H_4$) in about 4% yield by the reaction of $PbCl_2$ with $ArMgBr$ at $2^\circ C$. For a long period they were the only representatives of organic compounds of two-valent Pb. Unlike analogous compounds of the other elements of the silicon subgroup R_2M ($M = Si, Ge, Sn$), diarylplumbylenes could not be transformed into oligomers or polymers of the $(R_2M)_n$ type, but they easily disproportionated into Ar_4Pb and Pb at about $2^\circ C$. These data became additional proof of the inability of lead to form chains longer than $Pb-Pb-Pb$.

K. Biological Activity and Application of Organolead Compounds

Even the first investigators of organolead compounds encountered its harmful physiological action. Thus, for example, in 1860 Klippel^{1217,1218} reported that the vapors of hexaethyldiplumbane affected the mucous membranes and respiratory tract and caused a lachrymatory action and prolonged cold. Similarly, the hexaisoamyldiplumbane vapors irritated the mucous membranes. Klippel even tasted this substance and found that it caused a long-time scratching irritation of his tongue and even of his throat. It must be assumed that trialkylplumbanols, which were formed in the reaction of R_3PbPbR_3 with moisture from the air and CO_2 , caused all these symptoms. Krause and Pohland¹¹²³ (1922) felt the irritation action of the R_3PbX ($R = Alk$) dust. Browne and Reid¹²⁵⁰ (1927) and Gilman and coworkers^{1248,1399} (1930, 1931) found that the organolead compounds of the Et_3PbX type showed sternutatory and irritating actions and caused rhinitis symptoms.

In the end of the 1940s McCombie and Saunders synthesized large amounts of Et_3PbCl and felt the symptoms of a severe attack of influenza, which, however, disappeared at night and returned by day⁹⁷¹. High toxicity was the main effect of organolead compounds on living organisms. Obviously, the first researchers in the field felt this. It is noteworthy that the organolead derivatives turned out to be more toxic than inorganic lead compounds and even pure lead. From 1925 the toxicity of tetraethyllead started to be studied thoroughly because of its wide application as an antiknock of motor fuels^{1400,1401}. The toxic and physiological action of Et_4Pb and other organolead compounds was summarized in several monographs and reviews^{109,130,154,1402–1405}. The majority of these investigations were carried out in the second half of the 20th century.

Already in the first half of the 20th century, it was established that the first symptoms of Et_4Pb poisoning were a drop in body temperature, a marked decrease in blood pressure,

sleeplessness, headaches, nightmares and hallucinations. Higher doses of tetraethyllead caused insanity. The indicated emotional and nervous deviations indicated that the lipid-soluble Et_4Pb was absorbed rapidly by the soft and nervous tissues and concentrated in the latter. In 1925, Norris and Gettler¹⁴⁰⁶ found that a high concentration of lead occurred in brain, liver and kidney tissues. It was also established that tetraethyllead was able to penetrate human or animals through the integuments or by breathing its vapors. Extra large doses of Et_4Pb (in comparison with other highly toxic substances) caused a lethal outcome. Tetraethyllead was used as a poison in the mystery novel of Ellery Queen 'The Roman Hat Mystery'. The chronic effect of small doses of tetraethyllead due, for instance, to long respiration of its vapors or a lasting contact with its solutions in motor fuel (ethylated gasoline) resulted in serious poisoning. Removal of tetraethyllead and its metabolites from the body occurred very slowly owing to the resistance of Et_4Pb to hydrolysis and the insolubility of the resulting inorganic lead compounds in tissue liquids. Like tetraalkylstannanes, the toxicity of Et_4Pb depended on the cleavage of one C—Pb bond *in vivo* which resulted in the formation of the highly toxic cation Et_3Pb^+ ¹⁴⁰⁷.

An international arms race started shortly after World War II and was concerned with the creation of new types of chemical weapons, which inspired many prominent scientists in the USA, England, USSR and other countries to conduct investigations in this field. Organolead compounds were also involved in such studies and a search of their suppressing effect on human disturbances was started. In 1939–1941, Saunders in England carried out secret and extensive investigations for the Ministry of Supply with the aim of creating chemical weapons based on organolead compounds, having sternutatory and irritation action. Detailed data about these investigations were published^{1149, 1150, 1320, 1408–1410} in 1946–1950. They synthesized many compounds of the R_3PbX and R_2PbX_2 series. Remarkably, the authors and their coworker-volunteers tested the effects on themselves. They entered a special room, where an alcoholic solution of a tested compound in several concentrations was dispersed. The activity of the compound was determined by the time that the investigators could stay in the room. It was established that the derivatives of the R_3PbX ($\text{R} = \text{Alk}$; $\text{X} = \text{Hal}, \text{OH}, \text{OR}', \text{OOCR}', \text{SR}', \text{NHSO}_2\text{R}', \text{OCN}, \text{CN}, \text{SCN}, \text{N}(\text{CO})_2\text{C}_6\text{H}_4\text{-o}$ etc.) type were sternutators and irritating agents. The influence rate of the alkyl substituents R and X on the irritating effect of R_3PbX ⁹⁷¹ was also studied. On the whole, the activity of these compounds was increased for the following R substituents in the order: $\text{Me} < \text{Et} < \text{Bu} < \text{Pr}$. Hence, the Pr_3PbX compounds turned out to be the most active. Their representatives with $\text{X} = \text{OOCCH}=\text{CH}_2$, $\text{OOCCH}=\text{CHMe}$, $\text{OOCCH}_2\text{CH}_2\text{Cl}$, $\text{N}(\text{CO})_2\text{C}_6\text{H}_4\text{-o}$, $\text{NHSO}_2\text{C}_6\text{H}_4\text{Me-}p$ and NHSO_2Me were the most effective among the compounds mentioned above, and their unbearable concentration in air was lower than 1 ppm. The most powerful sternutators were $\text{Pr}_3\text{PbNHSO}_2\text{R}$ with $\text{R} = \text{CH}=\text{CH}_2$ and Ph , with an unbearable concentration of 0.1 ppm. All the investigators ran out of the room after 40 seconds when the compound with $\text{R} = \text{Ph}$ in the mentioned concentration was spread. Compounds of Ar_3PbX and R_2PbX_2 type had no effect at all or a little sternutatory action. It is noteworthy that the investigations of McCombie and Saunders, which had doubtless nonhumane but pragmatic aims, made a valuable contribution to the chemistry of organolead compounds. Their work resulted in the synthesis of many new substances of this class and led to new developments or improvements of their preparative methods. Analogous investigations were carried out in Gilman's laboratory on the other side of the Atlantic Ocean. The results were published in an article by Gilman, Spatz and Kolbezen¹³⁰⁸ only in 1953.

In 1928–1929, Evans and coworkers¹⁴¹¹ and Krause¹¹²⁶ started to investigate the possible use of organolead compounds as medicines, mainly against cancer.

In 1938, Schmidt¹³⁰⁴ examined their application against cancer from a historical aspect. He obtained many complex lead compounds of different types which did

not have the C–Pb bond. Along with them a series of organolead compounds Me_2PbCl_2 , $\text{Me}_2\text{Pb}(\text{OH})_2$, Me_3PbCl , Ph_4Pb , $(2,5\text{-Me}_2\text{C}_6\text{H}_3)_3\text{PbPb}(\text{C}_6\text{H}_3\text{Me}_2\text{-}2,5)_3$, $\text{Ph}_2\text{Pb}(\text{OOCMe})_2$, $\text{Ph}_2\text{Pb}(\text{OH})_2$, $(p\text{-O}_2\text{NC}_6\text{H}_4)_2\text{Pb}(\text{OH})_2$ and $(p\text{-H}_2\text{NC}_6\text{H}_4)_2\text{Pb}(\text{OH})_2$ was synthesized. These compounds were transformed into the corresponding water-soluble Na-aryllead pyrocatecholdisulfonates by the reaction with Na-pyrocatecholdisulfonate. Carcinogenic activities of the above seventeen synthesized compounds mentioned above were studied on mice carcinoma and partially on Brown–Pearce tumors. From all the compounds studied only the above-mentioned diarylsulfonatoplumbanes had a definite carcinogenic action. Testing radioactive lead compounds did not confirm the expected high activity. However, comparatively insufficient investigations in this field as well as studies of the effect of organolead compounds on plants and the possibility of using them in plant cultivation, as well as their use as components of antifouling paints, appeared only after 1970¹⁴¹². Nevertheless, even in 1952–1953 *N*-triethylplumbyl derivatives of phthalimide and phthalohydrazide were patented as fungicides^{1344,1345}. In 1959, a patent for the application of triethyl(diisobutylamino)plumbane as a herbicide¹³⁴⁶ was granted.

Practical use of organolead compounds will be hardly extended due to their high toxicity and the possibility of sustainable pollution of the environment by the lead compounds. In this connection it must be indicated that the production of tetraethyllead, which achieved 270,000 tons by 1964 only in the USA, started to be reduced at the end of the 20th century.

In the second half of the past century, there were numerous patents dealing with the application of organolead compounds as polymerization catalysts or as pesticides¹⁰⁹. However, they did not find any practical application. Regarding the same is true of Me_4Pb , which began to be used as an antiknock additive along with Et_4Pb in the 1960s.

V. CONCLUSION

The concepts and development of the chemistry of organic compounds of Group 14 of the Periodic Table heavy elements, i.e. germanium, tin and lead, are presented in a historical sequence in the earlier sections of this chapter. We have tried to tell the reader not only about the achievements of researchers in this field of organometallic chemistry, but also to give the names of pioneer researchers and their close successors. The development of organolead and organotin chemistry proceeded almost simultaneously and their study was actually synchronous in the middle of the 19th century. The investigations of organogermanium compounds were started in 1925.

The research interests in organic compounds of the elements above were not the same throughout the historical development of organometallic chemistry. The tin derivatives turned out to be the focus of interest in comparison with organogermaniums, which were less attractive, while organolead compounds attracted the least attention of scientists. Table 3 demonstrates these facts. The number of publications devoted to organic compounds of the elements of the silicon subgroup (mezoids) published in 1966 and in 1969⁴⁷ are presented. In these years the main fields of practical application of organic compounds of the silicon subgroup were determined.

It is not difficult to see that the number of published works generally corresponds to the importance of the elements in various fields of human activity. It is remarkable that the chemistry of organotin compounds was the most intensively developed in these years. In the 1960s, the rate of development of organosilicon chemistry was lower than that of the chemistry of organogermanium compounds. The dynamics of the research and progress in the field of organolead compounds both in the previous and subsequent years was relatively minimal. At the same time organolead compounds, the first of them being tetraethyllead, found practical application. There was a time when the industrial production of this antiknock additive of motor fuels exceeded the total output production

TABLE 3. The number of investigations devoted to organic compounds of the elements of the silicon subgroup, carried out in 1966 and in 1969

| | Number of articles | | Relative increase in the number of publications (%) |
|----|--------------------|------|---|
| | 1966 | 1969 | |
| Si | 615 | 823 | 34 |
| Ge | 148 | 208 | 40 |
| Sn | 207 | 537 | 159 |
| Pb | 71 | 82 | 15 |

of all the organotin and organogermanium compounds. At the end of the 20th century, organogermanium compounds found practical application as biologically active products.

Laboratory research on organic compounds of the silicon subgroup elements showed that they ought to be divided into two subgroups (dyads) in accordance with their similarity in chemical properties and biological activity. Silicon and germanium derivatives were placed in the first one while the tin and lead derivatives belong to the second.

Unlike this chapter, the history of organogermanium, organotin and organolead compounds has no end and will probably never have one. The initiation of various new research tendencies in this field of metalloorganic chemistry, which took shape at the end of the 20th and beginning of the 21st centuries, is a witness to this. Some of them are mentioned in Chapter 2. Nevertheless, it must be acknowledged with sorrow that the number of publications devoted to organic compounds of the elements reviewed in this chapter among the organometallic papers is decreasing more and more due to the rapidly growing interest in the transition metal organic derivatives and their complexes.

While working on this chapter, the first author recollected with pleasure, pride and a slight sadness his close acquaintance and friendly connections with many of the heroes of this narration whom he had met not only at international forums or in laboratories throughout the world, but also at home and in other everyday situations. They include H. Gilman, E. Rochow, R. West, D. Seyferth and A. MacDiarmid (USA); M. Schmidt, W. Neumann and H. Schmidbaur (Germany); K. A. Kocheshkov, A. N. Nesmeyanov, G. A. Razuvaev, O. M. Nefedov, V. F. Mironov, M. M. Koton, S. P. Kolesnikov and N. S. Vyazankin (Russia). At the same time, these reminiscences caused some sorrow in that the age of the author has become historical.

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This chapter is dedicated to friends and colleagues whose contribution to the organometallic chemistry of the last century was outstanding.

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